Electronic And Magnetic Properties Of Some Metal Chelates Of Substituted Thiosemi Carbazides

THESIS

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By

Har Narayan Singh

CERTIFICATE

This is to certify that the thesis entitled, "Electronic And Magnetic properties of some Metal Chelates of Substituted Thio semi carbazides" submitted for the Degree of Doctor of Philosophy of the University of Bundelkhand, Jhansi, (U.P.) is a record of bonafide research work carried out by Shri Har Narain Singh, Lecturer in Chemistry, Bipin Bihari College, Jhansi, under my guidance and supervision.

The work embodied in this thesis or a part hereof, has not been submitted for the award of any other Degree or Diploma. All the help and assistance received during the course of present investigations have been duly acknowledged.

(R.C.Saxena)4.2-82

Senior Lecturer,
Chemistry Department,
M.M. College, Modinagar-201204.

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Dedicated To My Divine

Mother

&

Father

C O N T E N T S

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Section - I -

GENERAL INTRODUCTION

The introduction of sulphur and nitrogen atoms in various organic compounds has resulted in important consequences towards the behaviour with the transition metals. Thiosemicarbazides and thiosemicarbazones are known to form a large number of complex compounds with transition and inner transition metal ion by bonding through sulphur and hydrazinic nitrogen. 2-Formyl Pyridine thiosemicarbazone and 1-Formyl isoquinoline thiosemicarbazone are known to possess antitumor activity[1]. Some complexes are also known to possess activity against tumor[2] influenza[3] and small pox[4].

Coordination compounds play an important role in chemistry of other elements having electro positive values i.e. elements which form ions or compounds in which they are electrophilic and hence capable of binding donor molecules. First transition series elements show variable valency. The facts responsible for this behaviour of transition metals are presence of an incomplete 3d- shell of electrons, the comparative ease of loss of two or more electrons by the metal atom and availability of d- orbitals for bond formation.

Considerable complexes of sulphur containing ligands are known[5-7]. Sulphur possess a position in the

middle of electronegative series $F > O > N > Cl > Br > I > S > Se > C > Te > P > As > Sb$. This electronegativity is greatly influenced by the groups attached to donor atoms. It is therefore evident that for a unidentate ligand the coordinating ability depends not only on the electronegativity but on the total dipole moment (μ) of the ligand $\mu = P + P^1 = P + \alpha E$ where P = the permanent dipole moment, P^1 = the induced dipole moment, α = the polarisability and the E = the inducing electro static field.

Livingstone[8] reviewed the complexes involving sulphur atom as donor viz. sulphides, thioethers, thiols and thiones. Sulphur atom has vacant d- orbitals which can be used for ($d\pi - d\pi$) bonding similar to those involved in transition metal having usual and unusually low oxidation states. Metal complexes of thiosemicarbazide and thiosemi-carbazone were studied at length by Campbell[9]. Livingstone and Akbar Ali[10] studied the carcinostatic and antiviral activity of sulphur nitrogen ligands and their complexes. Some papers concerning the magnetic behaviour of transition metal complexes of mercaptocarboxylic[11-13] acid, thiomalic[14-15] acid and thiosalicylic[16,17] acid are appeared in the literature. Sulphur give rise to both low and high spin complexes of transition metals. This is one of the explanation for anomalous magnetic properties of complexes formed from ligands involving sulphur as donor atom.

The magnetic behaviour of the lanthanides is fundamentally different from that of the d- block transition elements. The basic reason for the difference lies in the fact that the electrons responsible for the magnetic and spectral properties of lanthanide ions are 4f- electrons and the 4f- orbitals are very effectively shielded from interaction with external forces by the overlying $5S^2$ and $5p^6$ shells[19]. Therefore the state arising from various $4f^n$ configurations are only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in all its compounds. The magnetic properties of Lanthanides and their metal complexes have recently been reviewed by Sinha[19], Forsberg and Taylor[20].

The use of spectral and magnetic techniques have been widely made by Akbar Ali[21-28]. Campbell[29] and Ablov[30-33], cofreras et al.[34] have recently prepared and studied the Pseudo- Octahedral complexes of the type $\left[Cr (NCS)_n L(6-n) \right]$ where L is an organic ligand whose donor atom is (a) O (b) N (c) S (d) O and N (e) S and N, in most cases n = 4. Preti[35] reported the electronic spectra of several manganese (II) complexes with cyclic thiones, and found them octahedral. Agarwal[36] et al. reported the ultraviolet visible spectra of Rh (III), Ru (III), Pt (II), Pt(IV), Pd (II) and Pd (IV) complexes of 2, 4-di-thiouracil.

Campbell[37-40] et al. discussed the stereochemistry

of copper (II) and nickel (II) complexes of thiosemicarbazones on the basis of the metal ligand stretching vibrations ($400 - 80 cm^{-1}$). The X-sensitive bands are in the region of $250 cm^{-1}$ for chloride and $210 cm^{-1}$ for bromide. Gringras et al.[41] studied the chelate forming capacity of the thiosemicarbazones of some diketones. Bahr[42] suggested the structure of diacetyl-dithiosemicarbazone Cu (II). Several reviews[43-50] have been appeared which exclusively dealt with the ligand field perturbations having octahedral, tetrahedral, square planar and tetragonal distribution of ligands around the central ion. Perumareddi[51-56] has developed various energy equations for noncubic symmetry including quadrate, trigonal, and cylindrical ligand fields for d^2, d^3, d^7 and d^8 ions.

Infrared spectral measurements have been proved of immense utility in the determination of the structure of molecules and coordination compounds. Molecular vibrations shows the presence or absence of certain functional groups, ligand chain length, multiple bonding, isomerism or bound state of ligand and the degree of molecular symmetry[57-69]. Schiff bases and thioureas are amongst the most important nitrogen and sulphur containing ligands which show remarkable pharmacological activity and have wide biological applications[70]. Perhaps the group N - C - S is of considerable chemotherapeutic interest and is responsible for the pharmacological activity[71]. It has been indicated

that the microbiol activity of these compounds is due to their ability to chelate traces of metal ions[72]. Several Schiff bases complexes have been well investigated[73-77]. However only recently the attention has been directed to the complexes of the transition metals with monofunctional tridentate Schiff bases containing O, N, O and -O, N-S sequences[78-80], similarly 8-hydroxyquinoline and 4-hydroxy acridine[83] are also fungitoxic as they are suitable ligands to chelate the essential metals involved in fungal metabolism, as did N-Aryl/Hetero aryl-2, 2-Disubstituted azomethines which are known potential fungicides[84].

Multidentate ligands having the amine and the mercaptide groups have been reported to form quite stable chelate compounds with transition metals[85,86]. The amine and the mercapto group in 1,2 position behave as competitive nucleophiles, usually resulting in the formation of thiazolines. SUVOROKA et a.[87] have reported that the reaction of salicylaldehyde or its halogen derivatives with B-mercapto ethylamine produces a large percentage of the Schiff base rather than a thiazoline. Tandon[88] et al. reported the non transition metal complexes of salicyledene -2-mercapto-ethylamine; and suggested that the central atom possess un-common penta coordinate state[89-91].

Metals of first transition series particularly and various organic compounds containing N, S, or O and even elements of comparatively higher electronegativity such as As, P and Se have been used as ligands. In recent years

research on multidentate chelating agents[92-93] has been stimulated by a number of aspects such as their interesting and unique stereochemical properties, their wide spread occurence in living matter and many practical applications. With the advent of Multidentate ligands, coordination compounds bearing coordination number four, five, six, seven, eight and ten have been synthesized and studies. 2,4-Lutidine-1-oxide complexes of Lanthanide nitrates of the formula $Ln(NO_3)_3 (2,4-Luto)_4$ have been prepared and characterised[94,95] by chemical analysis, IR, NMR and conductance data. IR-data indicates both mono and bidentate nitrate groups in the complexes of La and Pr-nitrates and only bidentate nitrate groups in the other lanthanide complexes. The non electrolytic behaviour of the La- and Pr- nitrate complexes in acetonitrile in congunction with the IR data for the nitrate groups suggest a coordination number of 8 or 9 for the lanthanide ions according to whether, one or two nitrate groups are bidentate. Nair and Chacko[96] have reported the preparation and characterisation of complexes of 4-aminoantipyrine (aap) with lanthanide perchlorates[97] and nitrates[98] with the composition $\left[Ln (aap)_6 \right] (ClO_4)_3$ and $\left[Ln (aap)_3 (NO_3)_3 \right]$ respectively. Unlike other lanthanide complexes the lanthanide thiocyanates complexes are quite novel in that the lanthanide ions themselves fall into two groups (the lighter ones and the heavier ones) as regards their coordinating ability. The

lighter lanthanides (La, Pr, Nd and Sm) show a ligancy of
six and the heavier lanthanides (Gd and Dy) and Y show a
ligancy of nine. In fact the possible geometries of five,
seven and the complexes of higher coordination numbers
are such that the structure of the ligand and nature of
donor atoms play an important role in the stabilization
of transition metal complexes in the usual states, square
planar C_4V symmetry and Trigonal bipyramidal D_{3h} symmetry.

(a) Object and Scope :

In recent years the study of the chemistry of
thiosemicarbazides and thiosemicarbazones has been given
particular impetus because of their pharmacological and
industrial uses e.g. derivatives of thiosemicarbazides have
been used in the treatment of tuberculosis[99], influenza[100],
small pox[101] and certain kinds of tumour[102]. Their
activity has frequently been thought to be due to their
ability to chelate trace metal e.g. copper, the metal
complexes themselves being the active ingradient[103].
This is supported by the fact that Seleno semicarbazones
in which S-atom is replaced by selenium are more active
against fungi than the corresponding thiosemicarbazones.
This difference in activity is attributed to the formation
of metal complexes which would occur more readily in the
case of seleno semicarbazones[104]. p-acetamido benzaldehyde
thiosemicarbazone found use in tuberculosis. According to

the Liebermeiter the tuberculostat activity of the above
compounds can be enhanced with copper ions. The involvement
of metal ions in cancertherapy has been discussed by a
number of workers[105-107]. Istatin thiosemicarbazone
copper complex[108] has been used as an active antiviral
drug. In thiosemicarbazide and thiosemicarbazone the
toxicity may be due to $>N - \overset{|}{\underset{|}{C}} - S -$ grouping which is of consi-
derable chemotherapeutic interest and is perhaps responsible
for their pharmacological propteties[109]. Besides
pharmacological activities, thiosemicarbazide also possess
chelating ability due to dual potential sites at the thio-
ketonic sulphur and hydrazinic or azomethine nitrogen which
are ideally situated to be coordinated to the metal ions[110].
The denticity of such ligands can be increased by extending
the chain length of thiosemicarbazide by the introduction
of such groups as amide and benzene rings with phenolic
groups. By increasing the chain the idealized geometry
get disturbed to form tetragonally distorted complexes.

Attempts have also been made to study whether
the antifugal and antibacterial activities of such organic
ligands are enhanced reduced or remain unaffected after
complex formation. The effect of the metal ion and anion
attached to metal complexes have also been observed.

The metal complexes of the ligands derived from
α-Benzamido ortho chloro cinnamic acid; 5-acetyl-2-hydroxy-
Benzoic acid thiosemicarbazide and 1-hydroxy-2-naphthoic acid

thiosemicarbazide have not been studied so far though they
present many interesting features worth investigating.
To this end the present studies have been initiated. The
ligands contain thioketosulphur, azomethine nitrogen and
phenolic -OH as the potential donor sites to form five
or six membered ring chelates with heavy metal ions.
Besides throwing light on the coordinating ability of S,N,O
the antifugal and antibacterial activity of the ligands
and their metal complexes have been tested.

Antifungal and antibacterial activities :

Both ligands and the isolated complex were
screened for their antifungal activity against the test
fungus Helminthosporium sativum and Alternaria alternata
by linear growth measurement method. The prepared complexes
are also screened for antibacterial activity against the
bacteria Staphylococus aureus and Escherichiacoli by
employing the cut plate agar diffusion method. The anti-
bacterial results of the compounds showed a variable activity
against gram positive and gram negative bacteria.

Attempts have also been made to study whether
the antifungal and antibacterial activities of the ligands
are enhanced, reduced or remain unaffected after complex
formation.

(b) Antifungal and antibacterial activities :

Numerous complexes of thiosemicarbazide and

thiosemicarbazones have been reported in the literature[111-119] as pesticidal, fungicidal and against many diseases. The remarkable antituberculous activity of isoniazid[120-121] has initiated a sub-stantial amount of research on the transition metal complexes of pyridine carboxylic acid hydrazides and their derivatives. Some pyrazole based acid hydrazides have also been reported as pesticidal reagents[122]. In view of antituberculosis[123-129] and other pharmacological activities of metal thiosemicarbazides in biological systems, the physicochemical studies of the metal complexes are desired. A number of thiohydantoin derivatives are physio-logically active and some of them have been reported to possess anticovulsant[130], antibacterial[131], antifungal[132], antihypertensive[133] and such other properties. A variety of compounds both inorganic[134-136] and organic have long been used to prevent the fungal and bacterial attack. Although organic compounds have proved superior over those derived from inorganic sources but in a number of cases it has been observed that some compounds have increased activity when administered as metal complexes[137]. Recently it has been found that pyrimidine-2-thione[138] inhibits the synthesis of RNA leading to antitumour and antithyroid activity[139,140]. Mercapto triazoles resemble pyrimidine thione in having the identical donors. Thiadiazole ring is reported to display fungicidal[141] property by virtue

of $\rangle$N $-$ $\overset{|}{\underset{|}{C}}$ $-$ S $-$ linkage which is possible toxophore in many pesticides[142,143]. Several metal chelates are known to possess bactericidal[144] fungicidal[145] and antiviral[146] activity. Likewise it has been found that metal chelates are more fungitoxic than the chelating agents themselves in several cases[147]. Thiourea and thiocarbazone derivatives such as thiosemicarbazides and thiosemicarbazones have given particular impetus because of the discovery of their antifungal and antibacterial activities. It is known that the thiourea and its various derivatives have toxophoric $\rangle$N $-$ $\overset{|}{\underset{|}{C}}$ $-$ S $-$ grouping which of considerable chemotherapeutic interest and is perhaps responsible for their antifungal and antibacterial activity. Mason and Powell[148] point out that some chelates of oxine, notably those of copper are more fungitoxic than oxine alone. These observation led us to synthesis some new thiosemicarbazones and to investigate their antifungal activity if any.

Literature review on

(i) Electronic spectral studies :

Electronic structure of transition metal complexes have added much to our understanding during the past two decades[149-155] while a variety of experimental techniques have contributed to this progress, a central role has been played by electronic spectral spectroscopy in the visible

and ultraviolet spectral regions. Absorption experiments
have probably played a greater role than emission studies,
because the former yield information about the more excited
states than the latter. The electronic transition responsible
for the absorption bands frequently involve the rearrange-
ment of electrons with in the partially filled d-shells of
the central ion, although other types such as ligand to
metal or metal to ligand charge transfer transitions may
be observed. In recent years attention has been mainly
concentrated on the d-d transitions as the simple ideas of
ligand field theory suffice to interpret the broad features
of the spectrum. Many reviews have been appeared in which
the electronic spectral studies correlated with magnetic
and spectral properties of transition metal complexes derived
from nitrogen and oxygen donor ligands. The optical spectra
may be favourably described interms of a single ligand
field parameter Dq and the Racah's interelectronic repulsion
parameters A, B and C. These are generally viewed as empirical
parameters to be determined from experimental data. In
ligand field of symmetry lower than cubic such as tetragonal
and trigonal which arise by the super imposition of an axial
perturbation along the four fold or three fold axis of an
octahedral potential, two additional parameters $D\mu$ (μ is
S or σ thus giving rise to DS and $D\sigma$) $D\nu$ (ν is t and π
resulting in Dt and $D\pi$) where S and π refer to tetragonal
and σ and π are associated with the second order and the fourth

order spherical harmonics V_2^0 and V_4^0 respectively, and lead to an additional splitting of the otherwise degenerate electronic levels of the cubic symmetry. Thus inorder to define the spectra of tetragonally distorted complexes three parameters Dq, DS and Dt are needed. As a result in distorted octahedral systems or in mixed ligand complexes observations of the splittings of the cubic absorption bands can provide useful informations on the symmetry of the ligand fields.

Recently complete theory of paramagnetism in transition metal ions in the octahedral and tetrahedral d^3, d^4, d^5, d^6, d^7 electron configurations[156-159] and d^2 and d^8 electrons configurations in cubic (octahedral and tetrahedral), tetragonal (D_4h) and trigonal (D_3h) symmetry have been developed by konig and Kremer. The magnetic moment is a function of octahedral and tetrahedral ligand field splitting parameter Dq and the temperature for a fixed set of values of Racah parameters (B and C) spin orbit coupling parameter (λ) and the orbital reduction (K), whereas in D_4h and D_3h symmetry this quantity has been found to be a function of the parameters Dt or DT, respectively. With these deductions the effect of variation in parameters values of B, C, λ and K can be investigated. These results can be used in an accurate comparison of the experimental data with the theortical results.

The deductions arrived at by correlating the electronic and magnetic characteristics of transition metal complexes have been amply supported by the vibrational

spectra studies. The vibrational spectra especially the far IR region has been of specific importance in the assignment of the (M - L) vibrations. Very recently such studies led to differentiate between the stereochemistry, configuration and nature of the (M - L) bond in transition metal complexes[160-162].

From the above discussion it is quite clear that definite conclusion can be deduced regarding the stereochemistry, configuration, oxidation state of the central metal ion and the nature of metal donor link by correlating vibrational, electronic spectral and magnetic characteristics of transition metal ions both in cubic and noncubic fields.

In the present thesis an attempt has been made to apply the various theories atleast in semiquantitative manner supplemented by experimental observations to determine the structure and configuration of various metal chelate compounds with bulky ligands having N, O and S as the potential sites.

(ii) Magnetic studies :

The measurement of the magnetic moment has been one of the most important tools for predicting bond type oxidation state and stereochemistry in complex compounds. Since long this technique is in used for determining the structure of inorganic compounds[163-165]. Magnetic susceptibility measurements of paramagnetic and diamagnetic compounds have been very useful in revealing an accurate

description of many physicochemical properties of solids.
A single crystal in general shows directional properties
depending upon the inherent symmetry in its physical and
chemical nature and the magnetic susceptibility in different
directions of the crystal is different.

The anomalous magnetic behaviour observed in
the heavy transition metal complexes has been explained in
terms of

(i) the increase in the spin-orbit coupling constant 'λ'
of the metal involved.

(ii) The greater crystal field effects due to large energy
separation ($\triangle$ oh) between t_2g and eg orbitals.

(iii) the preponderance of intermediate form of coupling
over Russel-Saunder's coupling and

(iv) the influence of antiferro magnetic information.
Although magnetic studies[166-171] of complexes are being
carried out from a very long time, but the main attention
has been confined to the complexes of first row transition
metal ions. The inclusion of spin orbit coupling effects
into strong field configurations through out the transition
block by Kotani[172] made a considerable advance towards
explaining the observed large difference between magnetic
moment of first, second and third row transition elements
for a given configuration and their dependence on temperature.

In recent years coordination compounds in their
solid state have been reported to show deviations may be
categorised in such a way that one type occurs when the
electron pairing energy of a complex lies between the ligand

field strengths of possible high spin and low spin forms and results in a high spin $\rightleftharpoons$ low spin equilibrium which has been observed in number of systems[173-175]. A second type arises from the antiferromagnetic- interactions between the unpaired electrons of two or more metal atoms in a complex. Anomalous magnetic behaviour has also been observed in case of various transition metal complexes.

In several series of complexes deviations[176,177] from normal diamagnetic and paramagnetic behaviours have been found to be the result of the coordination of the metal atom of one molecule of a complex with the donor atoms of other molecules in such a way that the metal atom achieves pseudo octahedral configuration. Sangal et al.[178] have studied the Dipicolinic acid hydrazide complexes of oxovanadium at room temperature, the value of which lie in the range 1.65 - 1.73 B.M. These values are well within the range reported for oxovanadium (IV) complexes when the orbital contribution is completely quenched[179,180]. Cobalt (II) complexes of iminophosphoranes[181] show deviation of magnetic moment value from the spin only value of 3.88 B.M. but lie well within the limits (4.1 - 4.8 B.M.) expected for tetrahedral or approximately tetrahedral. The relatively high value of 'λ' the spin orbit coupling constants of the complexes indicate only a small amount of (CO - N) orbital overlap, confirming thus the weakness of the ligands.

2-Benzylpyridine N-oxide complexes with transition metal
perchlorates have been studied by speca and coworkers[182].
The magnetic moments of the new paramagnetic metal ion
complexes are normal for high spin d^5-d^8 compounds or the
d^9 configuration[183]. The moments of the Co^{+2} and Ni^{+2}
complexes are within the range of values reported for
other penta coordinated complexes of these metal ions with
aromatic amine[184-186] N - oxide. Naidu and Naidu[187]
while studying the thermal, spectral, ESR and magnetic
studies of complexes of copper (II) with O-hydroxychalcones
come a cross abnormal value of magnetic moments, which they
explained because of electron spin and orbital motion the
magnetic moment of Cu (II) may range from a value of 1.73 B.M.
(non orbital contribution) to 2.2 B.M. Different degrees
of orbital contribution are predicted in square planar and
tetrahedral environments. In the former geometry, no orbital
moment is expected by virtue of a non-degenerate ground
state. In the latter however an orbital contribution is
expected because the Jahn-Teller effect prevents a rigorously
degenerate ground state. Moments that contain large orbital
contributions have been used as evidence for pseudo tetrahedral
fields in bis (Cu (II) compounds[188-190].

(iii) <u>Infrared spectral studies</u> :

Infrared studies of organic compounds used as
ligands in preparing complexes have been made to identify
various modes of vibrations and hence their structures. This

technique has provided a powerful and useful unambigous method of structural determination for complexes of transition metals, Based on these studies many conclusions of the general nature and feasible with respect to ligand chain strength, presence or absence of certain, functional groups, multiple bonding, hydrogen bonding, isomerism, bound state of ligands, degree of symmetry, but lately it has been also possible to decide alternative stereochemistries[191-193].

In general the vibrations originating in the ligand appear in the high frequency region, and those originating in the coordinate bonds appear in the far i, r region. The analysis of low frequency spectra provide direct information about the coordination bounds, where as high frequency spectra reveal the secondary effect of coordination on the ligands. These secondary effects on coordination on ligand vibrations is the key to elicit whether coordination has taken place or not and if so then at what points. The most conclusive proof of coordination taking place is the appearance of several new modes of vibration e.g. $\nu(M - N)$, $\nu(M - S)$, $\nu(M - O)$ or metal-halogen in the far I-R region. The frequencies observed in infrared spectra are the functions of the mass as well as the force constant and on this account the band shifts are the function of metals. As a rule the direction of the shift depends upon relative electronegativities of L and X atoms in the ligand LX_n.

The data on metal-halogen stretching frequencies can be used to ascertain the dependance of v (M - X) vibrations on the oxidation number, mass and coordination number and on the stereochemistries, of complexes. Making use of symmetry arguments, relationship between v (M - X) vibrations and stereochemistry has been established. Such studies are of particular importance where the metal atom has a closed shell of valence electrons and hence the electronic absorption spectra and magnetism yield no conclusive information regarding the stereochemistry.

However, it may be mentioned that the (M - L) stetching vibrations are rarely pure, coupling with other normal modes of vibrations of the same symmetry in the molecule is generally expected . The title metal-halogen, metal- sulphur, or metal- nitrogen used should be taken to infer that a particular absorption band arises primarily but not necessarily totally, from such as a normal coordinate.

Several papers[194-196] have been reported concerning the assignments possibility of coordination, metal- ligand bond nature, stability of nitrogen and or oxygen donor complexes of metal ions belonging to all the three transition series. Because of relative heaviness of metal atom and low bond order of the coordinate links both r(M - N) and r (M - O) frequencies have been reported to appear in the lower frequency region $\sim 500 \text{cm}^{-1}$ and $\sim 300 \text{cm}^{-1}$ respectively in a large number of complexes.

Narang et al. have isolated the complexes of amino pyrine with metal (II) perchlorates and found that it acts a bidentate ligand and belongs to the pyrazole group. The negative shift[197-198] in V (C = 0) by $\sim$ 50cm^{-1} and V(C - N) by $\sim$ 30cm^{-1} in copper (II) complex suggest that aminopyrine has two sites of coordination with metal. In other complexes however, a strong bond at 1090cm^{-1} due to ionic perchlorate[199] overlaps the V(C - N) vibration. The perchlorate vibrations between 1085 - 1090cm^{-1} and 620 - 625cm^{-1} are due to V_3 and V_4 modes respectively. A weak band V_1 is observed at 940cm^{-1} in the complexes and it is due to crystal field effect. The absence of splitting of these bands indicates tetrahedral symmetry of the percheorate and hence its ionic nature. The coordinated water absorbs between 3400 - 3500cm^{-1} r(0 - H) in Fe (II), Ni (II) and Cu (II) complexes. Bending vibration of H_2O overlaps with the carbonyl frequency. The H_2O rocking frequencies occur between 835 - 845cm^{-1} indicating that water is coordinated to the metal ion[200]. The non ligand M - 0 and M - N vibrations are observed at 450 - 400cm^{-1} and 330 - 300cm^{-1} respectively[201,202].

Section - II

Metal complexes of thiosemicarbazide of alpha-benzamido-ortho chlorocinnamic acid.

(A) Literature survey

(B) Preparation of thiosemicarbazide of alpha-Benzamido-ortho chlorocinnamic Acid.

(C) Divalent metal complexes of Manganese nickel, cobalt and copper.

(D) Trivalent metal complexes of chromium and Iron.

(E) Tetravalent metal complexes of titanium (IV) and oxovanadium (IV)

Section – II– <u>Metal complexes of thiosemicarbazide of α –</u>

<u>Benzamido-ortho-chlorocinnamic Acid.</u>

(a) <u>Literature survey</u>

<u>Introduction :</u>

There has been recent interest in the chemistry

of ligands of the type containing N, O and S – as donor

atoms. These molecules are suitable for a study of the

stoichiometry and stereochemistry of their complexes formed.

Various complexes of d– transition metals have been prepared

and characterised, the diimine behaves as a bidentate ligand,

however complexes with the diimine monodentate have also

been isolated[203-207]. Pachauri and Rastogi[208] prepared

Cu (II), Pd (II), Pt (II) complexes of tridentate schiff

bases derived from 2– (2'–aminoethyl) Pyridine and salicylal-

dehyde or its derivatives (X–Salaep), O–OH–acetophenone

and O–OH–propiophenone have been obtained as coloured

crystalline solids. On the basis of analytical, magnetic

susceptibility, IR and electronic spectral data, the complexes

have been assigned square planar geometry. IR studies show

that the metal are coordinated through the nitrogen atoms

of the imine group and heterocyclic ring and the oxygen atom

of a phenolic group. Dubey and Wazir[209] evaluated the

stability constants of number of metal ions and found the

order is as follows $Cu^{+2} > Ni^{+2} > Co^{+2} > Zn^{+2} > Mn^{+2}$ except for

the ferrous complex, this sequence is in agreement with

the order given by Mellor and Maley[210, 211]. Abnormally

high stabilities for the Fe (II) complexes have been

observed in many cases, particularly with aromatic ligands

e.g. riboflanin[212] etc. The effect has been atributed to

the resonance stabilisation energy of Fe (II) complexes on

coordination with a ligand having aromatic ring system[213].

The spin- spin coupled oxovanadium (IV) complexes have been

prepared by syamal and Kale[214] utilising, the ligands

containing (O,O), (O,N), (O,S), S,S), (O,N,S), (O,N,O) and

(O,O,O) donor sites, and found, most of them are magnetically

condensed, non crystalline powders precluding their structure

determination by single crystal X - ray.

Cobalt (II) has a $3d^7$ nonbonding shell and usually

forms complexes having regular tetrahedral symmetry as

expected for the $(eg)^4 (t_2g)^3$ configuration. It uses $4S4p^3$

hybrid orbitals for bonding. But the coordination number

may increase to five or six involving $4S4p^3 4d$ or $4S4p^3 4d^2$

orbitals depending on the experimental conditions and the

polarizabilities of the ligand used. Several mixed ligand

complexes of Cobalt (II), Cd (II), Ni (II) and Zn (II) have

been reported[215-218]. Underhill and Billing reported[219]

some copper complexes with a number of nitrogen donor ligands

and discussed their structure on the basis of electronic

spectra. Uncertainity prevails regarding the exact ordering

of energy levels in Cu (II) complexes having crystal field

of D_4h symmetry. Both B_1g and B_2g states have been assigned
as the ground state for 3d- electronic configuration.
Whatever be the splitting diagram, three transitions for
Cu (II) in D_4h symmetry are expected. It has been suggested [220,221]
that greenish colours and absorptions in the vicnity of
$1430cm^{-1}$ are indicative of a penta or hexa coordinated
Cu (II) whilst four coordinated Cu (II) is characterised
by brown to violet colour with absorption peaks close to
$18200cm^{-1}$. Mn (III) compounds have been much less studied
than those of other trivalent transition metal ions, because
of a strong tendency of Mn (III) to get reduced to Mn (II).
Thiosemicarbazide with more than one coordinating centres
can be used as suitable ligands to prepare stable Mn (III)
chelates. As the Mn^{+3} ion can be easily reduced charge
transfer will be from the ligand to metal assignable to
$\pi \longrightarrow t_2$ transition.

The coordination chemistry of Pd^{+2} has been
extensively investigated[222]. A major portion of the work
carried out on Pd^{+2} and Pt (IV) complexes deals with nitrogen
containing ligands[223], and only limited number of references
are available on their complexes with sulphur containing
ligand[224]. Spacu and Camboli[225] on the basis of IR
data indicated the presence of (Pd-S) bond in the mixed ligand
complexes of Pd (II).

Following Malatesta and Cariello[226,227] a number
of workers[228] have initiated investigation on Pt (0)

complexes and found them to be tetrahedral. Recently the spectroscopic studies on rare earth chelates have assumed considerable importance because of their use as Laser materials[229-232]. The first pulsed laser action from chelates was reported by Lempicki and Samelson in europiun benzoylacetonate at $6130A^{\circ}$. Considerable research interest has been exhibited in these materials and the complexity of their coordination chemistry is now becoming more fully understood[233]. The hydrated lanthanide acetates have several coordination possibilities[234] and the acetate ion may be either monodentate, bidentate or dimeric ligand. In crystalline state recently[235] it has been established that in haloacetates of lanthanides the dimeric haloacetate group plays an important role in determination of their structures. This has been verified from their molecular weight studies.

The most important features of the transition metal ion complexes is the exhibition of varied stereochemistries, namely square planar, tetrahedral and octahedral. In recent years a number of tetragonally distorted complexes of these metal ions have been reported with plausible experimental and theortical evidence. In several cases the methods have been given to calculate the degree of distortion on the basis of electronic spectral bands.

(b) (i) <u>Preparation of Thiosemicarbazide of Alpha-Benzamido-</u>
<u>ortho chlorocinnamic Acid</u> :

Hippuric Acid 4.5 gm; Fused sodium acetate 2.05 gm;
o-chlorobenzaldehyde 2.804 ml; and Acetic anhydride 7.16 ml.

The above reactants (1 : 1 : 1 : 3 mols) were
taken in 100 ml round bottom flask, fitted with an air
condenser and heated over a water bath for forty five minutes.
Yellowish white solid was formed after forty five minutes
on heating. The reaction mixture was left overnight. It
was then treated with 10% solution of sodium bicarbonate
and filtered. The residue was shaken with hot water and
filtered again. The filtrate was rejected and the residue
was treated with alcohol and filtered. The filtrate was
rejected and the residue was dried over porous plate.

5.0 gm of the yellowish white substance obtained
above and about 2.0 gm of potassium hydroxide and 125 ml
of water were heated in a 250 ml R.B. flask on a water bath
for about two hours. The solution was then cooled and
filtered. To the filtrate concentrated hydrochloric acid
was added gradually and with constant stirring. To complete
the precipitation hydrochloric acid was added in slight excess.
It was cooled and filtered through Buchner funnel at the
filter pump and dried on the porous plate. The compound
was recrystallized from water and alcohol. Yield 5.8 gm
M.P. - 220°C mol. formula - ($C_{16}H_{12}O_3NCl$)

Cl — CH = C - C = O   <u>Hydrolysis in presence of KOH</u> →

with the azlactone ring: N = C(C$_6$H$_5$)-O
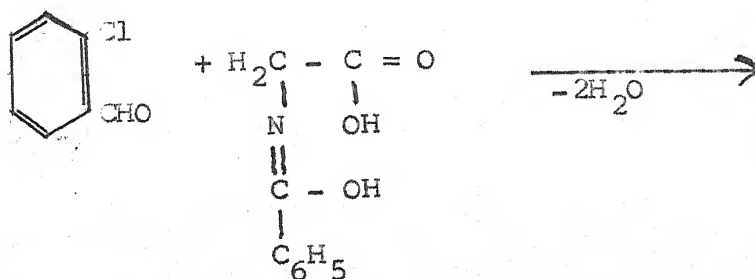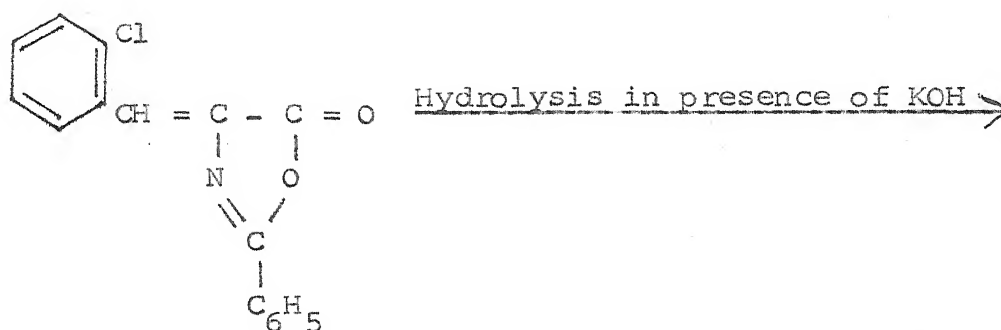
(O-chloro benzylidene Hippuric Acid Azlactone)

Cl — CH = C(COOK)(NHCOC$_6$H$_5$)

↓ Conc. HCl
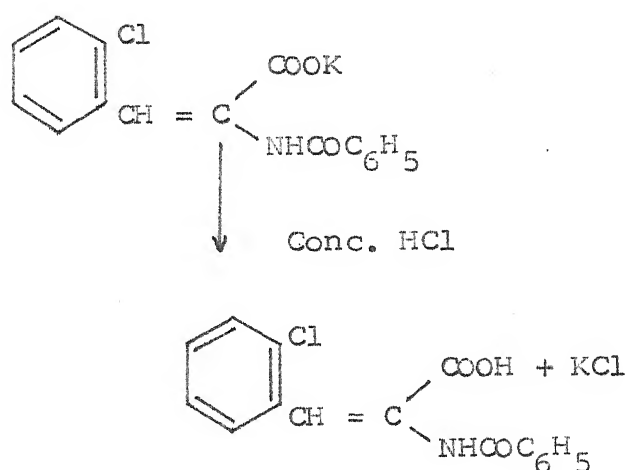
Cl — CH = C(COOH)(NHCOC$_6$H$_5$) + KCl

($\measuredangle$ - Benzamido-o-chlorocinnamic Acid)

(ii) <u>Preparation of Acid Hydrazide</u> :

Acid hydrazide of $\measuredangle$ -Benzamido-o-chlorocinnamic Acid was prepared by refluxing a mixture of the methyl ester of the above acid (1.0 M) and hydrazine hydrate (1.5 M - 99-100%) for three hours the said hydrazide was recrystallised from hot water.

(iii) <u>Synthesis of thiosemicarbazide of $\measuredangle$ -Benzamido-o-chloro-cinnamic Acid</u> :

Acid hydrazide of $\measuredangle$ -Benzamido-o-chlorocinnamic Acid (1.0 M) was suspended in liquor ammonia (d- 0.88; 200ml)

and carbon disulphide (45 ml cooled to 0°C) was added with
stirring in 15 ml out of 45 ml portion. The temperature of
the reaction mixture was kept below 30°C by external cooling.
Ethanol (100 ml) 95% was then introduced into the flask.
In addition 30 ml of carbon disulphide was added, followed
by 100 ml of ethanol (95%) when all the additions were comp-
leted, the reaction mixture which was kept in a water bath
was stirred with the help of a mechanical stirrer for an
hour. An aqueous solution of sodium monochloroacetate
(1.0M) obtained by neutralization of monochloroacetic acid
with sodium carbonate was then added and the heat was found
to develop to the warm solution hydrazine hydrate (60 ml,
99-100%) was added. After the reaction mixture was shaken
for ten minutes, it was filtered and the filterate was
heated on a water bath to one half of its volume and cooled.
On cooling the concentrated reaction mixture overnight.
Crystals of thiosemicarbazide of alpha benzamido-O-chloro-
cinnamic acid were obtained, the thiosemicarbazide was
filtered and recrystallised from glacial acetic acid
(M.P. 105°C) (Mol. formula - ($C_{17}H_{16}N_5O_2ClS$)

Calculated -   C-52.38   H-4.11   N-17.97   S-8.22   Cl-9.11

Found   - C-53.68   H-4.22   N-8.76   Cl-9.40

Cl–C₆H₄–CH = C(COOH)(NHCOC₆H₅) + CH₃OH / H₂SO₄ → Cl–C₆H₄–CH = C(COOCH₃)(NHCOC₆H₅)

$$\text{Cl–C}_6\text{H}_4\text{–CH} = \text{C}\begin{array}{l}\text{COOH}\\ \text{NHCOC}_6\text{H}_5\end{array} \; + \; \frac{\text{CH}_3\text{OH}}{\text{H}_2\text{SO}_4} \longrightarrow \; \text{Cl–C}_6\text{H}_4\text{–CH} = \text{C}\begin{array}{l}\text{COOCH}_3\\ \text{NHCOC}_6\text{H}_5\end{array}$$

$$+ \; NH_2 - NH_2 \; \downarrow$$

$$\text{Cl–C}_6\text{H}_4\text{–CH} = \text{C}\begin{array}{l}\text{CONHNH}_2\\ \text{NHCOC}_6\text{H}_5\end{array} \; + \; CH_3OH \; + \; \text{liquid ammonia} \; + \; ClCH_2COONa \; + \; H_2N - NH_2 \; + CS_2$$

$$\downarrow$$

$$\text{Cl–C}_6\text{H}_4\text{–CH} = \text{C}\begin{array}{l}\text{CONHNH} - \overset{\text{S}}{\underset{}{\text{C}}} - \text{NH} - \text{NH}_2\\ \text{NHCOC}_6\text{H}_5\end{array}$$
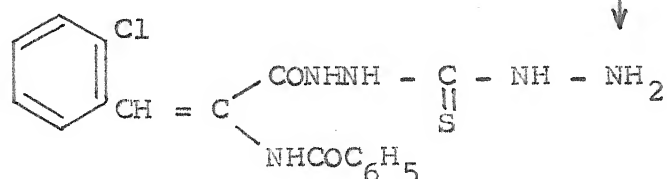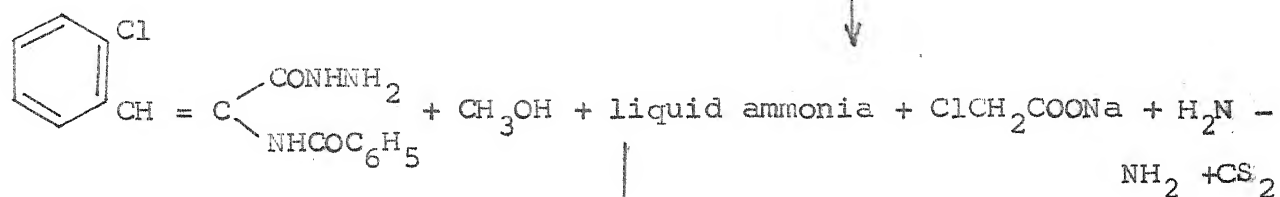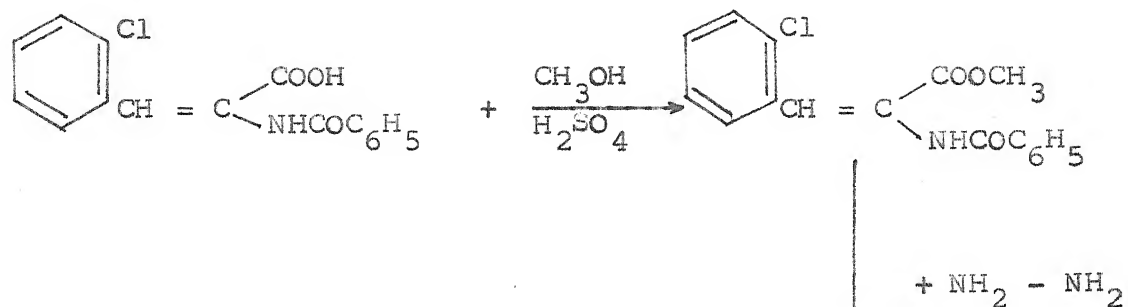
(c) Divalent metal complexes

Mono (α-Benzamido-O-chlorocinnamic acid - thiosemicarbazide) manganese (II) chloride monohydrate.

On mixing 20 ml of 0.05 M ethanolic solution of the organic ligand with 20 ml of 1.0 M manganese (II) chloride tetrahydrate in ethanol a yellowish brown precipitate was obtained. The mixture was refluxed on water bath, cooled and filtered, washed with small amounts of water and ethanol. The analysis correspond to the formula :

$$\left[Mn(C_{17}H_{16}N_5O_2ClS)(Cl_2) \, H_2O \right]$$
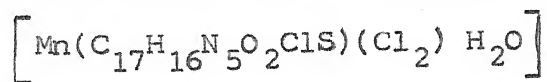
	Calculated	Found
Mn -	10.30	10.60
C -	38.24	39.31
H -	3.37	3.45
Cl -	19.78	20.41
N -	13.12	13.62

Cu (II), Ni (II) and Co (II) complexes :

These complexes were prepared by directly mixing required quantities of ligand and metal solutions in ethanol. The coloured compound which separated in each case was filtered off, washed with water and alcohol and dried over fused calcium chloride. The analytical data of the complexes corresponds to the formula :

$$\left[Cu(C_{17}H_{16}N_5O_2ClS) \ Cl_2 \cdot H_2O \right] H_2O$$

$$\left[Ni(C_{17}H_{16}N_5O_2ClS) \ SO_4 \cdot H_2O \right]$$

$$\left[Co(C_{17}H_{16}N_5O_2ClS) \ Cl_2 \right]$$
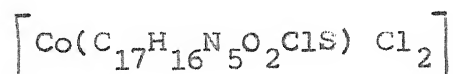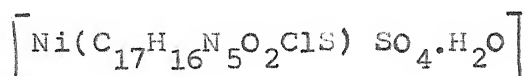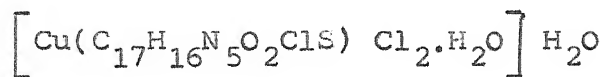
	% Calculated	% Found
Cu –	11.35	11.63
H –	3.57	3.47
N –	12.50	12.94
S –	5.71	5.50
Cl –	18.84	19.56
Ni –	10.44	10.80
H –	3.20	3.30
N –	12.45	12.08
S –	11.38	11.40
Cl –	6.31	6.56
Co –	11.78	11.35
H –	3.16	3.08
N –	13.86	13.48
S –	6.02	6.16
Cl –	21.32	20.50

The magnetic data are given in table (1 – 2).

The electronic spectral bands, their assignments and relevant ligand field parameters are cited in tables (1 - 2). Table (3 - 4) records the infrared spectral data. Figure (1 - 5) shows the infrared spectra of ligand, and its Mn^{+2}, Cu^{+2}, Co^{+2} and Ni^{+2} complexes.

Results and Discussion :

Analytical results show 1 : 1 metal to ligand stoichiometry in all the complexes.

Magnetic and electronic spectral studies

Manganese (II) complex :

Complex show magnetic moment value of 5.85 B.M. which is consistent with a $6A_1g$ ground state for Mn (II) ion. The electronic spectra of the isolated complex show four energy bands at 19600, 23470, 27804 and $32400cm^{-1}$ which are assigned to the sextet-quartet transitions, $4T_1g(G)$, $4T_2g(G)$ and $4Eg(G)$, $4A_1g(G)$ respectively. The values of 10Dq, B and C have been calculated, using equations suggested by Figgis which comes out to be 8976, 816 and 3672.

Copper (II) complex :

The low magnetic moment of the complex suggest antiferromagnetic[236,237] interaction between the Cu (II) ions arising from dimerisation or polymerisation in the

Table – 1

Magnetic, electronic spectral and other relevant ligand field parameters in cm^{-1}.

Complex	Observed bands (cm^{-1})	Assignments		ueff B.M.	10Dq	Racah parameters B ; C		Nephe-lauxetic ratio
$[Mn(C_{17}H_{16}N_5O_2Cl.S)(Cl_2).H_2O]$	19600	$6A_1g$	$\longrightarrow 4T_1g(G)$	5.85	8976	816.66	3672	0.85
	23470		$\longrightarrow 4T_2g(G)$					
	27804		$\longrightarrow 4EG.4A_1g(G)$					
	32400		$\longrightarrow 4T_1g(P)$					
$[Cu(C_{17}H_{16}N_5O_2ClS)(Cl_2.H_2O)]H_2O$	14.48KK	$2B_1g \longrightarrow 2B_2g$		1.70	49.20			
	11.00KK	$2B_1g \longrightarrow 2A_1g$						

solid state either through $Cu^{+2} - Cu^{+2}$ interaction or through ligand participation.

The electronic spectra of the complex is characterised by a broad asymmetric band appearing in the range 11.00 - 16.0 KK, ruled out the possibility of a tetrahedral structure. Since no major spectral band is observed below 10 KK, although it is possible for distortion to occur such that a buckled square planar configuration could give rise to absorption between 10 - 16 KK.

In D_4h symmetry[238] three transitions from the ground state viz $2B_1g \longrightarrow 2A_1g(V_1)$, $2B_1g \longrightarrow 2B_2g(V_2)$ and $2B_1g \longrightarrow 2Eg(V_3)$ are predicted from the energy level diagram. The splitting of the octahedral $2Eg$ and $2T_2g$ states increases with tetrahedral compounds of the crystal field. Thus the closely packed broad transition may be due octahedral symmetry. The approximate value of 10Dq has been calculated using the expression :

$$10 \ Dq = V_3 - \frac{V_1}{2} - \frac{1}{3} (V_3 - V_2).$$

Cobalt (II) complex :

Typical tetrahedral Co (II) complexes have[239] magnetic moments in the range 4.4 - 4.8 (B.M) while the range is 2.1 - 2.9 B.M for square planar[240] Co (II) complexes.

The magnetic moment of the complex lie in the

range 4.35 B.M at room temperature, and is slightly lower than the range suggested for high spin four five or six coordinate complexes. The range suggested for high spin five coordinate complex is 4.2 - 4.6 B.M. The value observed for the present complex appear to approach this range which may either conform to square pyramidal, trigonal bipyramidal or intermediate geometries. However, the magnetic moments do not distinguish between the various stereochemistries.

In tetrahedral geometry the Co (II) complexes exhibit three spin allowed transitions viz $4A_2 \longrightarrow 4T_2$ ($3000 - 5000 cm^{-1}$), $4A_2 \longrightarrow 4T_1(F)$ ($4000 - 8000 cm^{-1}$) and $4A_2 \longrightarrow 4T_1(P)$ ($14000 - 17000 cm^{-1}$), where as in the octahedral stereochemistry the bands lie in the range 7500 - 10000 $\left[4T_1 g \longrightarrow 4T_2 g(F) \right]$ (V_1) around 15000 and $17000 cm^{-1}$ $\left[4T_1 g \longrightarrow 4A_2 g(F) \right]$ (V_2) and $18000 - 19000 cm^{-1}$ $\left[4T_1 g \longrightarrow 4T_1 g(P) \right]$ (V_3) and in some cases $22000 - 28000 cm^{-1}$ (charge transfer).

The electronic spectra of the complex show three bands in the region $\sim$ 9000 - 10500, 15000 - 17800 and $22000 - 24000 cm^{-1}$ and can be assigned to $4A_2(F) \longrightarrow 4B_1$, $4A_2(F) \longrightarrow 4E(F)$ and $4A_2(F) \longrightarrow 4A_2(P)$ respectively. The spectra is similar to other five coordinate cobalt complexes in which the assignments have been made on the basis of C_4V symmetry of the complexes[241,242].

Table – 2

Magnetic and Electronic spectral data of the complexes.

Complex	Observed bands (cm⁻¹)	Assignments	Dq	B	DQ	DS	DT	$\frac{DT}{DQ}$	dσ	ueff B.M.
$[Co(C_{17}H_{16}N_5O_2Cl\ S)Cl_2]$	9700	$4A_2(F) \rightarrow 4B_1$	1134	1182	18974	5642	10315	0.54	217	4.45
	16360	$4A_2(F) \rightarrow 4E(F)$								
	23430	$4A_2(F) \rightarrow 4A_2(P)$								
		$(\beta - 1.21)$								
		Dt = 761								
		DS = 806								
$[Ni(C_{17}H_{16}N_5O_2ClS)SO_4 \cdot H_2O]$		$3A_2g(F) \rightarrow 3T_2g(F)$ (v₁)	1111	1207	19609	7777	9244	0.47	387	3.14
		$3A_2g(F) \rightarrow 3T_1g(F)$ (v₂)								
		$3A_2g(F) \rightarrow 3T_1g(P)$ (v₃)								
(v₁) – 11110		Dt = 682								
(v₂) – 17080		DS = Dqz = 1111								
(v₃) – 25370										
(v₄) – X										

The energy level sequence for a C_4V symmetry can be drawn as dxz, dyz $<$ dxy $<$ dz^2 $<$ dx^2 — y^2. In a square pyramid the highest energy level dx^2 — y^2 would be lowered and the lowest energy level dxz, dyz would be considerably raised, thus the total spread of the levels in cobalt (II) markedly decrease on distortion.

The normalised spherical harmonic (NSH)
Hamiltonian and its applications to the present complexes:

Lever et al.[243] applied the newly developed theory of normalised spherical harmonic (NSH) Hamiltonian to find out the absolute ligand field parameters designated as DQ, DS, DT, DQA and DQE in conjunction with Racah inter electronic parameters B and C. These parameters along with the ratio DT/DQ which measures the degree of distortion project the true stereochemistry and nature of bonding in cubic and noncubic complexes.

These parameters have been fully capitalised to distinguish them from the conventional ligand field parameters Dq, Dq^E, Dq^A, DS and Dt and the relationship has been established between them. The advantage of NSH Hamiltonian parameters are (a) it takes into account an off diagonal contribution to Dt and (b) these parameters are independent on the coordinate system used for calculations and may be compared with the crystal field or angular overlap model to determine restrictions on values.

The parameters of the classically used Hamiltonian
and the NSH Hamiltonian parameters are related by

$$DS = -7DS$$

$$DT = \frac{7\sqrt{15}}{2} (Dt)$$

$$DQ = (6\sqrt{21})(Dq) - \frac{7\sqrt{21}}{2} (Dt)$$

It is noted that with this Hamiltonian the tetragonal
distortion splits the eg and t_2g levels of the octatedron
in a fashion which obeys the centre of gravity rule for
both DS and DT in contradiction to the classical approach.

In the limit octahedral symmetry when DS and DT
are zero the tensor Hamiltonian fields values of DQ which
are greater than those of calssically used Hamiltonian by
the factor $(6\sqrt{21})$. Two additional parameters derived from
the spectra of tetragonal molecules such as ME_4A_2 are DqE
and DqA, the magnitudes of the crystal field parameter in
the hypothetical octahedral ME_6 and MA_6 respectively[244,245].

In the NSH Hamiltonian these quantities are related
to the classical one through[246]

$$DQ = (\frac{1}{6})(4DQ^E + 2DQ^A)$$

$$DT = (\frac{1}{3})(\frac{\sqrt{5}}{\sqrt{7}})(DQ^E - DQ^A)$$

$$= (\frac{1}{2})(\frac{\sqrt{5}}{\sqrt{7}})(DQ - DQ^A)$$

$$= (\frac{\sqrt{5}}{\sqrt{7}})(DQ^E - DQ)$$

These equations make it clear that DQ is a measure of the average ligand field experienced by the metal ion, unlike the classical Dq which is a measure of the inplane ligand field. The values of DQ, DS, DT, Dq and B- have been evaluated and are put in the tabular form. The ratio of $\frac{DT}{DQ}$ provides a measure of degree of distortion. The DQ^A has the significance of the field experienced by the metal ion along Z- axis. It is actually an average of the axial ligand field due to the absence of a ligand in the sixth position. In such a case where the field strength in the sixth position is zero, the DQ^A has a magnitude of half the field strength of the axial ligand.

The NSH absolute parameters can also be related to the Mcclure molecular parameters as

$$d\sigma = (\tfrac{1}{28})\ (6DS - (\sqrt{15})\ DT$$

$$d\pi = (\tfrac{1}{14})\ (3DS + 2(\sqrt{5}/\sqrt{3})\ DT$$

where $d\sigma$ represents the difference between the antibonding powers of the Z (σZ) ligand and the σ antibonding power of the (X - y) plane ligand σL, $d\pi$ is thus similarly defines

$$d\sigma = \sigma Z - \sigma L$$

$$d\pi = \pi z - \pi L$$

The negative value of $d\sigma$ indicate that the σ antibonding capability of equatorial ligand is more than that of the axial ligand and since $d\pi$ is positive, the π - bonding ability

of axial ligand is more than equatorial ligands.

Nickel (II) complex :

The magnetic properties of nickel (II) complexes have been extensively studied. Many octahedral complexes of nickel (II) have been found to have a magnetic moment between 2.90 - 3.8 B.M. which is slightly higher than the spin only value for two unpaired electrons and is beleived to be due to some 'mixing in' of upper state via spin-orbit coupling. The magnetic moment of the present complex is 3.14 B.M. which is well with in the range of octahedral nickel (II) complexes.

Six coordinate nickel (II) complexes exhibit a spectrum involving three spin-allowed transitions to the $3T_2g(F)$, $3T_1g(F)$ and $3T_1g(P)$ levels. These occur in the range of 7000 - 11000cm^{-1} (V_1), 15000 - 19000cm^{-1}(V_3) and 25000 - 29000cm^{-1}(V_4) regions respectively. In addition to these bands, two spin forbidden bands 1Eg and 1T$_2$g are frequently observed.

The present Ni (II) complex show three bands in their electronic spectra favouring an octahedral stereo-chemistry. The bands may be assigned to the transitions $3A_2g \longrightarrow 3T_2g(V_1)$, $\longrightarrow$ 1Eg(D) (spin forbidden) and $\longrightarrow 3T_2g(F)(V_2)$. The intense charge transfer absorptions occuring above 25000cm^{-1} possibly masked the expected higher

energy bond $3A_2g \longrightarrow 3T_1g(P)$ (V_3). The position of V_3 band has been calculated[247,248] to be at $27600 cm^{-1}$. The values of Dq, B and the ratio V_2/V_1 which are around 1111; 1207 $1.53 cm^{-1}$ respectively are in good agreement with those of other similar complexes and confirm the octahedral structures for the complex[249-251]. The nephelauxetic ratio for the complex lie at 1.15 suggesting a high degree of covalency. An approximate value of spin orbit coupling constant has been obtained using $\lambda = 2.7 \times B^2/10Dq = 354$. The experimental room temperature ueff value agree well with the calculated value of magnetic moment using the relationship ueff = u S.O $(1 - \frac{4\lambda}{10Dq})$ and comes out to be 3.60 B.M.

Infrared studies :

The IR spectra of the ligand as well as those of their complexes with divalent metal ions along with assignments for most of the major and important bands are given in table (3 - 4). The assignments are based on the corresponding thiosemicarbazides, thiosemicarbazones[252-254] thiocarbohydra-zides and complexes derived from them. The bands at 1280 and $850 cm^{-1}$ in the free ligands are due to $V(C = S)$. The other characteristic IR bands appearing at 1540(S), 1280(W), 890(S) and $670 cm^{-1}$ may be assigned to amide (I), amide (III), V (N - N) of the hydrazide residue. The negative shift of the amide I (appearing at $1620 - 1640 cm^{-1}$) by about $10 - 30 cm^{-1}$ and the positive shift of the amide (III) band (appearing
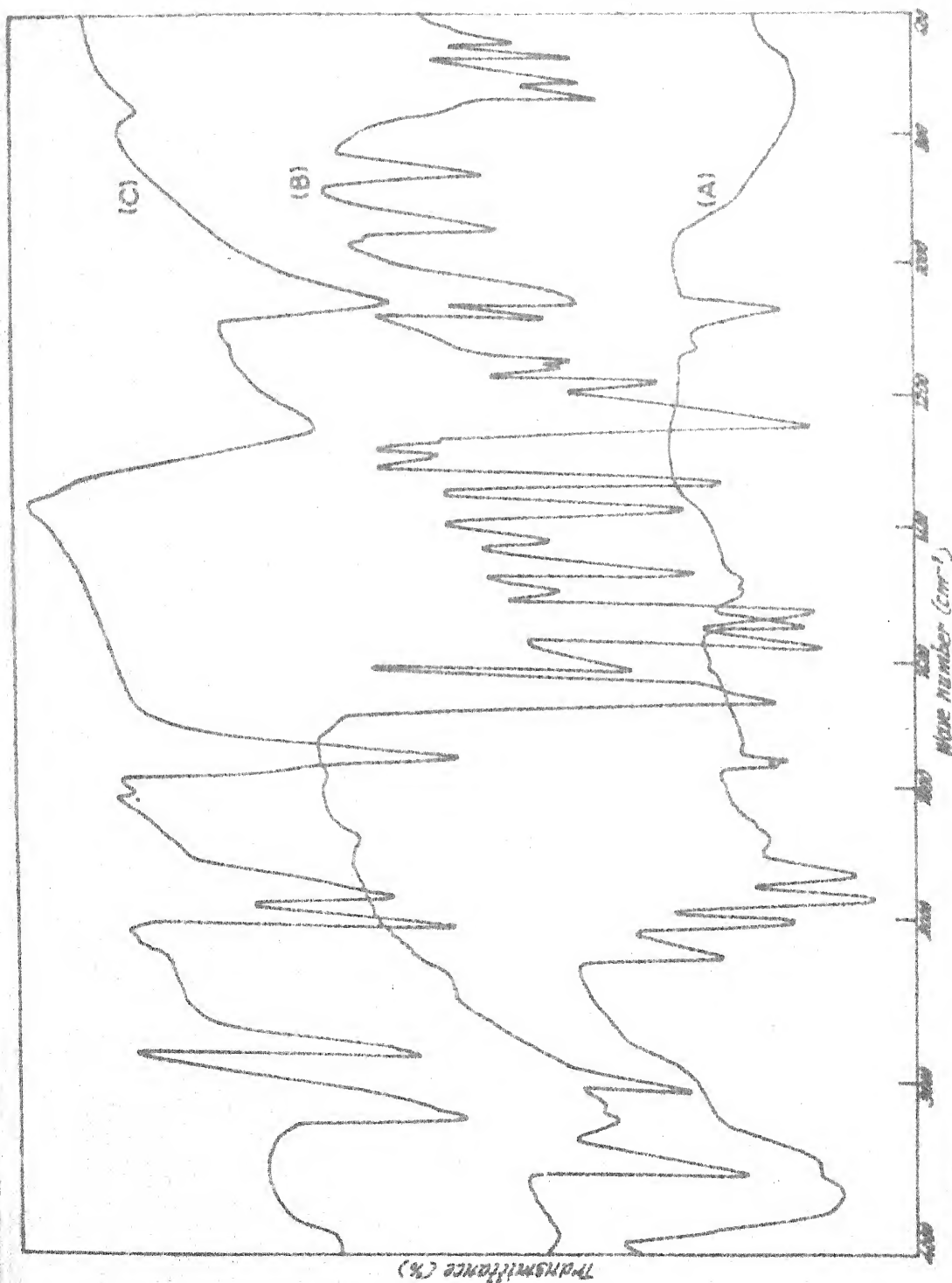
I.R. Spectra of :

(A) – Thio semcarbazide of α–benzomido – o – chlorocinnamic acid.
(B) – Thio semicarbazide of 5–acetyl–2–OH–benzoic acid.
(C) – Thio semicarbazide of 1–OH–2–naphthoic acid.

[C₁₇ H₁₆ N₅O₂ClS]

Fig.1 _ I.R.Spectrum of thio semicarbazide of ∝-benzamide- α-chlorocinnamic acid.

[Mn(C17H16N5O2Cl5)Cl2]·H2O

Wave number (cm-1)

Absorbance
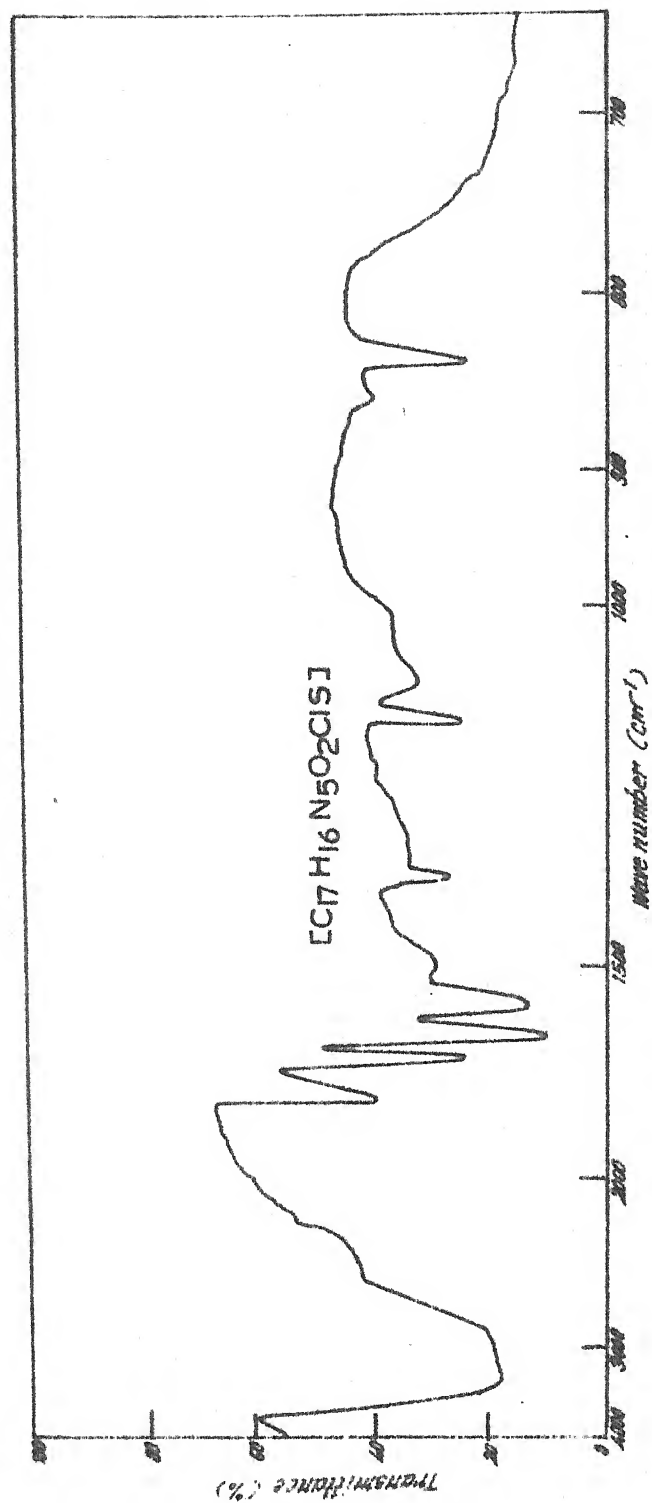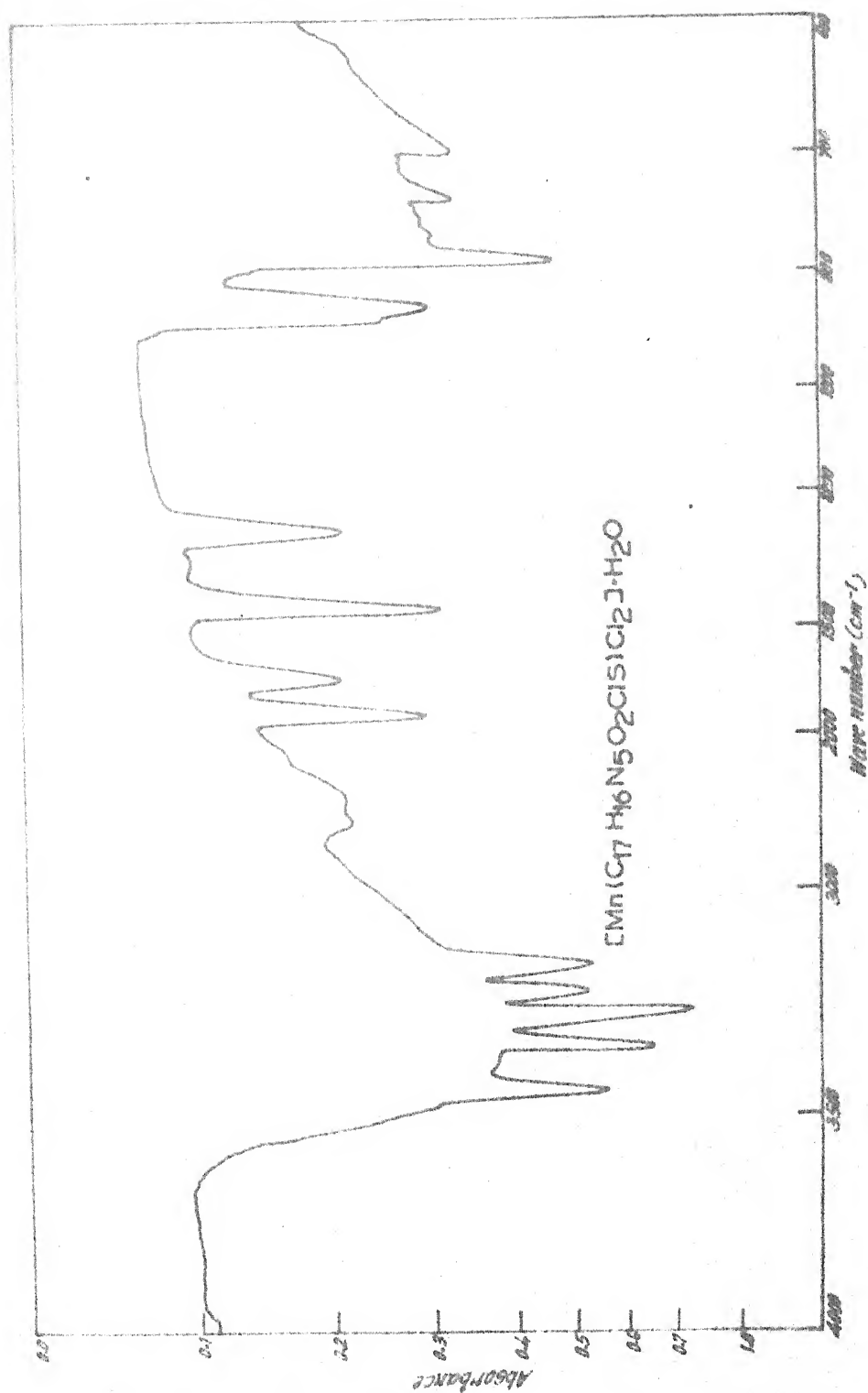
Fig-2

at 1280 - 1300cm^{-1}) by about 20 - 40cm^{-1} in the IR spectra of the complexes compared to those of the free ligand points to the participation of amide- nitrogen in bonding. In the region 1550 - 1650cm^{-1} there is a wide shifting in the frequency of (C = O) group indicating its participation in coordination. Carbonyl stretching frequency occurs in the complexes at 1630cm^{-1} and its negative shift from 1700cm^{-1} (that of free ligand) is indicative of coordination.

Further the (C = S) frequency also get lowered as compared to the uncomplexed ligand indicate $>$C = S is also the possible bonding site[256-259]. Since no band due to S-H near 2580cm^{-1} appear in the spectra of the ligand, this show that the ligand remain in thione form, atleast in the solid state[260]. The ligand show two ν(N -H) bands at 3260 and 3340cm^{-1} which do not undergo any appericable shift on complex formation indicating non coordination of NH$_2$ group. The ligand also show two moderately strong bands at 1490 and 1300cm^{-1}, assigned[261] as VCN $+ \alpha$NH$_2$ $+ \nu$CS. The complexes displays band at 3490 and 3350cm^{-1}, indicating that the complex contains water of crystallisation. Three bands around 820, 650 and 400 in the spectra of the complexes have been assigned to the coordinated water molecule, and the last band may be due to metal oxygen bond. The band appearing around 3150 also gets broaden perhaps due to the presence of coordinated water molecule. The infrared spectra of the

isolated complexes show newly formed low frequency bands assignable to V (M - O) and V (M - N) around 500 and 450cm^{-1}. Such assignments for V (M - O) and V (M - N) have also been supported by earlier workers[262]. The bands at still lower frequencies i.e. at 300-280cm^{-1} have been assigned to V (M - S).

The frequencies of absorption bands due to sulphate group in the complex are consistent with those normally associated with bidentate chelating sulphate[263,264] groups.

[Cu(C$_{17}$ H$_{16}$ N$_5$ O$_2$ Cl S)Cl$_2$·H$_2$O]·H$_2$O
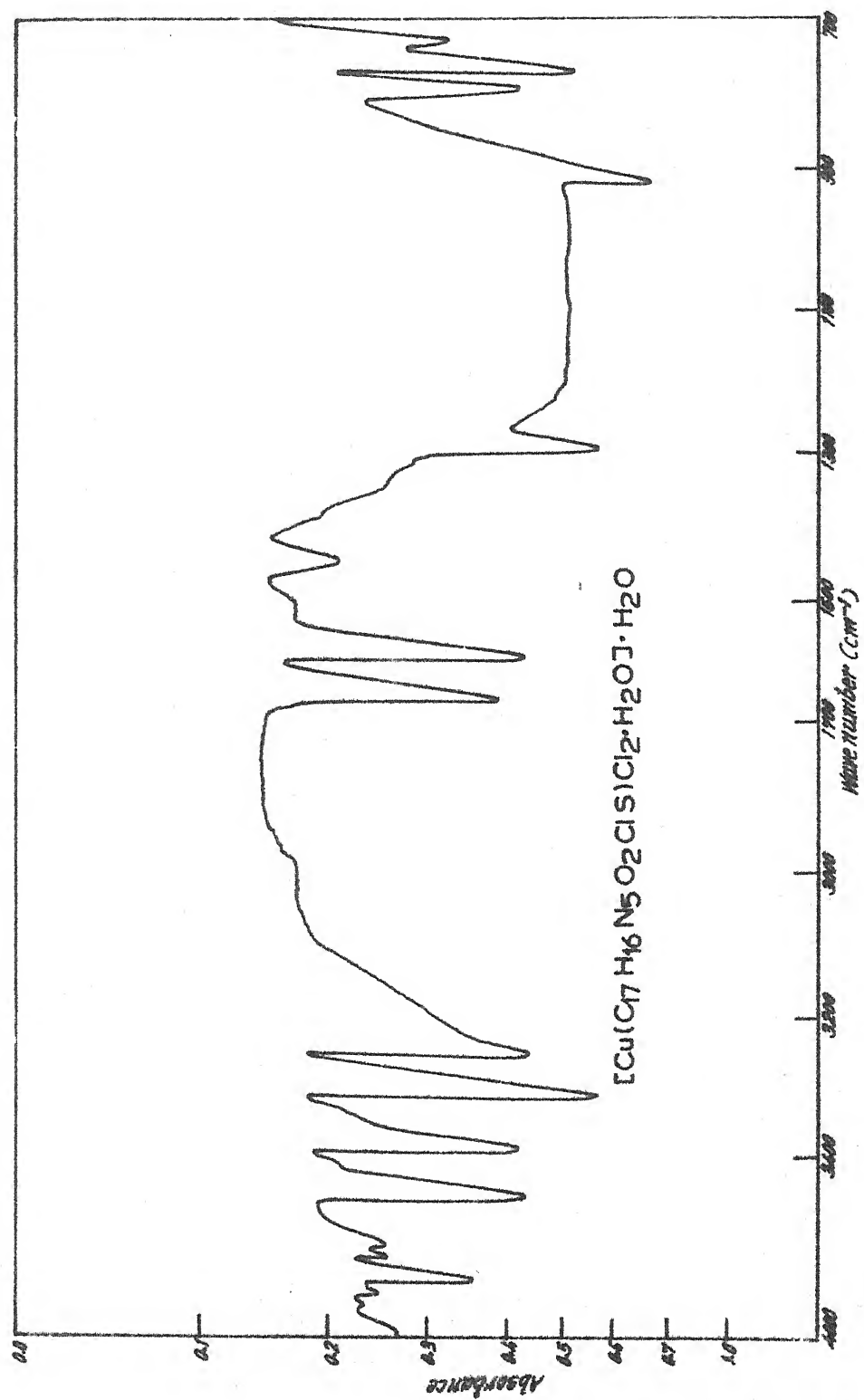
Fig.3

Table - 3

IR spectra of the organic ligand and its divalent complexes.

$C_{17}H_{16}N_5O_2ClS$	$[Mn(C_{17}H_{16}N_5O_2ClS)(Cl_2).H_2O]$	$[Cu(C_{17}H_{16}N_5O_2Cl.S)Cl_2.H_2O]H_2O$	Assignments
850(w)	810(w)	820(m)	$>C=S$
1640(S)	1600(S)	1680(S)	$-CONH$
3290(S), 3250(m)	3280(S)	3285(S)	NH and $-NH_2$(Sh)
1450(m), 1310(S)	1480(m)	1480(m)	$\nu_{CN} + \delta NH_2 + CS$
1640(S), 3490(m)	1610(S), 3400(m)	1620(S), 3420(m)	$\nu(N-H)$ of amide I
–	3490(m), 930(w)	3490(w), 930(m)	$\delta(H_2O)$ of coordinated
–		800(w), 750(w)	$\delta_w H_2O$
1300(S)	1340(S)	1320(S)	(CONH) amide III
3340(S), 3260(m)	3340(S), 3250(m)	3340(S)	(NH_2)
Fig (1)	Fig (2)	Fig (3)	

$[Co(C_{17}H_{46}N_5O_2ClS)Cl_2]$

Transmittance (%)

Wave number (cm^{-1})

Fig.4

[Ni(C17 H16 N5 O2Cl 5)(SO4) H2O]

Wave number (cm⁻¹)

Transmittance (%)

Fig. 5

Table – 4

Infrared spectral assignments of Co (II) and Ni (II) complexes.

$(C_{17}H_{16}N_5O_2ClS)$	$\left[Co(C_{17}H_{16}N_5O_2ClS)Cl_2\right]$	$\left[Ni(C_{17}H_{16}N_5O_2ClS)(SO_4)H_2O\right]$	Assignments
850(w)	830(w)	810(w)	$\rangle C = S$
1640(S), 1700	1600(S)	1670(S)	– CONH
3290(S), 3250(m)	3270(S)	3250(m)	– NH and NH_2 (St)
1450(m), 1310(S)	1450(m)	1440(m)	$\nu(CN + \delta NH_2 + CS)$
1640(S)	1600(S)	1600(w)	$\nu(N – H)$ of amide I
–	–	3310(w)	$\delta r(H_2O)$ coordinated
–	–	870(w)	$\delta w(H_2O)$
1280(m)	1310(S)	1300(m)	r(CONH) amide III
3340(S), 3260(Sh)	3340(S)	3340(S)	$r(NH_2)$
Fig (A)	Fig (4)	Fig (5)	

(d) Trivalent metal complexes :

A number of complexes of trivalent chromium, manganese (III) iron (III) and cobalt (III) have been isolated and characterised with the help of their magnetic and spectral properties. A variety of chromium complexes including octahedral, tetrahedral, and trigonal symmetry are known.

Iron (III) is known to form both octahedral and tetrahedral complexes depending upon the nature of the ligand fields. In the present studies thiosemicarbazide of α-benzamido-ortho-chlorocinnamic acid has been found to form spin free octahedral complexes with these metal ions.

(i) Trichloro mono-α-benzamido-o-chlorocinnamic Acid chromium (III) complex :

A solution of chromium (III) chloride (0.02 mole) in ethanol was added to a solution of ligand (0.02 mole) in the same solvent. After refluxing the mixture for about an hour the coloured precipitate obtained, which was filtered off, and washed with water and dried over potassium hydroxide in a vacuum desicator. The complex did not melt upto 280°C. The analysis revealed the formula $\left[Cr(C_{17}H_{16}N_5O_2ClS)Cl_3 \right]$

		Calculated	Found
Cr	-	9.49	9.16
H	-	2.92	2.84
N	-	12.77	13.12
Cl	-	25.91	26.50

(ii) <u>Trichloro mono (α-benzamido-ortho-chlorocinnamic acid)</u>

    <u>thiosemicarbazide Iron (III) complex</u> :

On mixing 20 ml of ethanolic solution of iron (III)
chloride (0.02 mole) with 20 ml of the ligand in the same
solvent instatneously give coloured precipitate. It was
refluxed for about half an hour, and filtered gave brown
precipitate. It did not decompose upto $280^{\circ}C$. The analysis
revealed its formula to be $\left[Fe(C_{17}H_{16}N_5O_2ClS)Cl_3 \right] 2H_2O$

	Calculated	Found
Fe –	9.50	9.20
H –	3.40	3.52
N –	11.91	12.34
Cl –	24.16	25.12

The magnetic moments, electronic spectral bands
and the relevant ligand field parameters are given in table – 5.
In table (6) infrared spectral data are recorded. Fig (6) and
Fig (7) represent the I.R. spectra of the α-benzamido-o-chloro-
cinnamic acid thiosemicarbazide and its complexes of chromium
(III) and iron (III) respectively.

Results and Discussion :

Chromium (III) complexes with different ligands
have been extensively studied and the magnetic moments are
reported to be in the range 3.50 – 3.88 B.M. at room[265,266]
temperature. The chromium (III) with an electronic configura-
tion of d^3 is expected to show a paramagnetism corresponding

to three unpaired electrons. The complex under study possess 3.65 (B.M) magnetic moment which is close to spin only value for octahedral complexes of chromium (III).

In cubic fields only one ligand field parameter Dq is needed to describe the spectra where as in the quadrate field to more ligand field parameters DS and Dt are introduced, because of the added axial[267] fields. The axial ligand field Dt is very similar to Dq in that both are matrix elements of the fourth order harmonic potential. In the limit of crystal field formalism it can be shown that

$$Dt = \frac{4}{7} \left[Dq(x) - Dq(y) \right] \quad \text{for an octahedral complex.}$$

For an octahedral environment three spin allowed (d-d) transitions, $4A_2g(F) \longrightarrow 4T_2g(F)(V_1); \longrightarrow 4T_1g(F)(V_2)$ and $\longrightarrow 4T_1g(P)(V_3)$, are expected in d^3 system such as chromium (III) but V_3 is generally hidden under charge transfer and interligand transitions in the near ultraviolet spectra. The first band occurs at 17000 and the second one at 24100 cm^{-1}, while the third band at 37000(V_3) in addition there is a low energy spin forbidden band at 11370 - 12140 cm^{-1}. The energies of the two higher bands are calculated from the following equation

$$V_{2,3} = (7.5B_{35} + 15Dq) \quad \frac{1}{2} \left[225B_{35}^2 + (10Dq)^2 - 180Dq \; B_{35} \right]^{\frac{1}{2}} \quad \text{-- (1)}$$

The Racah parameter B- may be calculated by four methods depending on the transition energies used[268] which differ simply by the band on which they fit.

Table – 5

Magnetic and electronic spectral studies on chromium (III) and iron (III) complexes.

Compound	Bands	Assignments	10Dq	V2	V3	Racah Parameter B	Nephelauxetic Para-lauxetic effect B35	β	B	ueff (B.M)
$[Cr(C_{17}H_{16}N_5O_2ClS)Cl_3]$	$^4A_2g(F) \rightarrow {}^4T_2g(F)(V_1)$	17000	17000	28280	31680	673	0.73	71.93	0.79	3.65
	$\rightarrow {}^4T_1g(F)(V_2)$	24100								
	$\rightarrow {}^4T_1g(P)(V_3)$	37000								
	charge transfer	12140								
$[Fe(C_{17}H_{16}N_5O_2ClS)Cl_3]$ $2H_2O$	$^6A_1g(G) \rightarrow {}^4T_1g(G)$	14200	6508	–	–	591.66	–	–	–	6.00
	$\rightarrow {}^4T_2g(G)$	15600								
	$\rightarrow {}^4A_1g(G)$	27340								

(a) $B_{35} = (2V_1^2 + V_2^2 - 3V_1V_2) / (15V_2 - 27V_1)$

(Fitting the second band)

(b) $B_{35} = (2V_1^2 + V_3^2 - 3V_1V_3) / (15V_3 - 27V_1)$

(fitting the third band)

(c) $B_{35} = (V_2 + V_3 - 3V_1) / 15$ (fitting the sum of the second and third band.)

(d) $B_{35} = \frac{1}{75} \left[3V_1 + \left[25(V_3 - V_2)^2 - 16V_1 \right]^{\frac{1}{2}} \right]$

(fitting the difference of third and second band)

But since (V_1, V_2 and V_3) all the three transitions have been observed in the complexes reported here in the equation (c) has been used to calculate[269] B^1. Low value of B_{35} is believed to be indicative of both σ and π -type delocalisation. V_1 directly give the value of 10Dq.

Crystal field theory can not be used to predict the spin forbidden transition frequencies it only the quartet-quartet transitions are known and hence other transition energies have been computed. An attempt has been made to calculate the spin orbit coupling constant[270] using

$$\lambda = \frac{2.7 \times B_{35}^2}{10 \ Dq}$$

$$\lambda = 0.0110 \ (B_{35} + 1.080)^3 + 0.0062$$

The values for the covalency parameters have also been calculated as $\lambda/90$. The band which is obtained at 12140 is spin forbidden transition 2E. An attempt has been made

to calculate this transition energy using the expression[271]

$$E\ (2E)\ =\ 9B\ +\ 3C\ -\ \frac{50B^2_{35}}{10Dq}$$ which comes out to be (12801).

This confirms the above assignments.

Iron (III) complex :

The magnetic moment observed for the complex is 6.00 B.M at room temperature, which confirm a high spin type octahedral[272,273] geometry around iron (III).

The electronic spectrum of the present complex show three absorption bands at 14200, 15600, and 27340cm^{-1}. These bands may be assigned to the transition $6A_1g(G) \longrightarrow 4T_1g(G)$; $\longrightarrow 4T_2g(G)$ and $\longrightarrow 4A_1g(G)$. 4Eg(G) respectively. The values of 10Dq and B have been calculated using the relationship $\frac{Dq}{B} = 1.1$; $\frac{6A_1g \rightarrow 4T_1g(G)}{B} = 24$ and comes out to be 6508 and 591.66 respectively.

IR - spectral studies :

The principal infrared bands and their assignments are shown in table (6). From a comparison of the spectra of the ligand and its complexes, the nature of coordination of the ligand to the metal ion can be very well understood. The amide I band appearing at 1700cm^{-1} in the ligand is lowered by 20cm^{-1} on complexation, where as the amide (IV) and amide (VI) bands shift in opposite direction, this shows that oxygen of the secondary amide group is coordinated to the metal[274,275]. The bands appearing at 3200, 1640 and

$1300cm^{-1}$, represent the CONH amide - CO and N - H bonding. In the metal chelates the frequency of CONH has lowered to 1610 and $1605cm^{-1}$ indicating involvement of amide nitrogen in complexation. Appearance of bands in the narrow ranges 410 - 420 and $405 - 410cm^{-1}$ suggest metal nitrogen bonding in the chelates. Formation of (M - O) is evidenced by the appearance of bands in the ranges $500 - 530cm^{-1}$.

The band at about $1610cm^{-1}$ in the free ligand which has been assigned to NH_2 deformations[276] does not changed in the metal complexes. The bands appearing around 1280 and $850cm^{-1}$ in the ligand may be assigned to C = S stretching vibrations. In the metal complexes these bands are weakened and lowered. This indicate the coordination of the ligand through sulphur atom.

A broad peak around $3500cm^{-1}$ confirming the presence of water molecules, and a very weak band near $780cm^{-1}$ could be assigned to rocking vibration of water attached to iron.

It is thus inferred that amido nitrogen and oxygen as well thione sulphur are the bonding sites of the ligand molecule in both the complexes.

[Cr(C$_{17}$H$_{16}$N$_5$O$_2$ClS)Cl$_3$]

Wave number (cm^{-1})

Absorbance
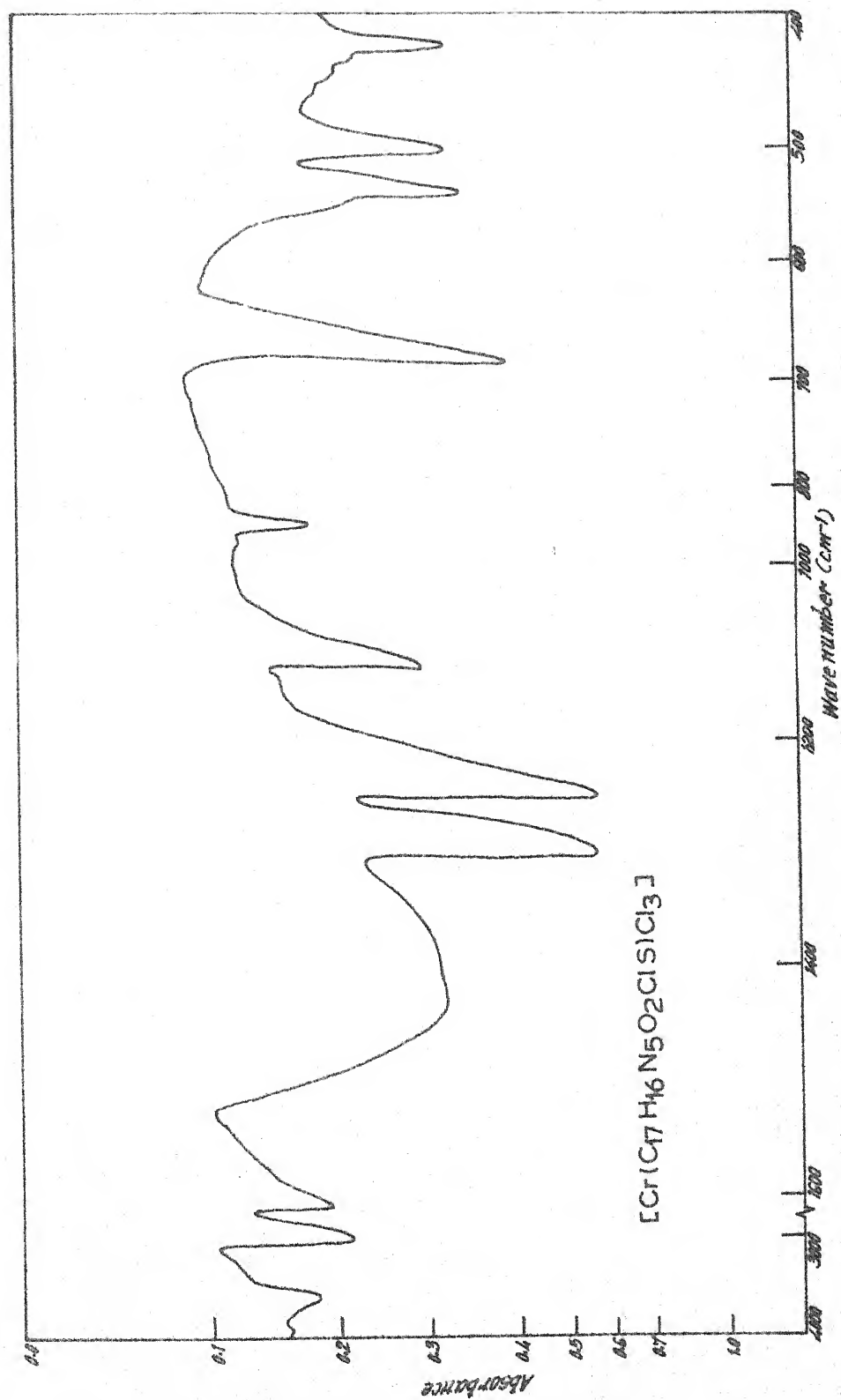
Fig.6

Table - 6

Infrared spectral assignments of chromium (III) and iron (III)

complexes.

$[Cr(C_{17}H_{16}N_5O_2ClS)Cl_3]$	$[Fe(C_{17}H_{16}N_5O_2ClS)Cl_3]$ $2H_2O$	Assignments
1680(m)	1670(vs)	Amide I
690 w.Sh	685(Sh)	Amide IV
560(S)	560(S)	Amide VI
1630(m)	1635(m)	Amide II
1300(b)	1310(S)	Amide III + $V_4(B_2)$ + ligand
1130(m)	1130(m)	ring deformation
1610(S)	1605 (S)	$>$ CONH
410 (S)	420 (m)	$V(M - N)$
500 (w)	520 (w)	$V(M - O)$
1250 (w)	1270(w)	$>$ C = S
830 (m)	840(m)	
Fig (6)	Fig (7)	

[Fe(C$_{17}$H$_{16}$N$_5$O$_2$ClS)Cl$_3$]

Wave number (cm^{-1})

Transmittance (%)

Fig.-7

(e) <u>Tetravalent metal complexes</u> :

Tetravelent titanium is shown to possess varied stereochemistry ranging from octahedral to dodecahedral. Six, seven and eight coordinate complexes of tetravalent titanium are known[277-279]. The possibility of obtaining complexes containing unusual coordination number of five, seven and eight increases with multidentate ligands involving S, N and O as potential donor atoms. Interest in the chemistry of tetravalent oxovanadium species, Vo^{+2} have been increasing perhaps due to the fact that Vo^{+2} is most stable and persistent diatomic cation available for varied complex ion research. N- substituted thioureas[280-285] have been extensively studied regarding the site of metal ligand bonding, covalency parameters and structure. Very few reporters are available on oxovanadium (IV) halide or thiocyanate complexes. In the present part of the chapter few complexes on titanium (IV) and oxovanadium (IV) have been reported.

The vanadyl thiocynate was prepared by metathesis of $VoCl_2$ and KCNS in ethanolic medium and the precipitated KCl was filtered off keeping $Vo(SCN)_2$ in site.

<u>Titanium (IV) BCAT complex</u> :

Equimolar quantities of titanium (IV) chloride in aquo-ethanol and the ligand in ethanol were mixed and the mixture was refluxed for about an hour. Separated solid was filtered washed with water and dried in vacuum at room

temperature. Data on elemental analysis correspond to

formula $\left[Ti(C_{17}H_{16}N_5O_2ClS)Cl_3 \right]$ $Cl.H_2O$

		Calculated	Found
Ti	-	8.02	8.34
C	-	34.15	33.10
N	-	11.72	12.17
S	-	5.36	5.21

Oxovanadium (IV) complexes :

It was prepared by mixing $Vo(SCN)_2$ solution and ligand solution in 1 : 1 molar ratio, a dark coloured complex thus separated was filtered washed with water and dried under vacuum. Analytical data corresponds to the formula $\left[Vo(C_{17}H_{16}N_5O_2ClS)(NCS)_2 \ H_2O \right]$

Magnetic and electronic spectral studies :

Magnetic susceptibility measurements at room temperature ($300K^O$) on powder form of the complex show that it is dimagnetic in nature. Titanium (IV) being a d^O system is relatively unimportant from the ligand field spectra point of view. The electronic spectra show strong bands in the region (30000 - 34000) and (36000 - 43000cm^{-1}). These bands have their origin in charge transfer phenomenon and lower higher energy bands can be assigned to $(1t_1)^6 \longrightarrow (1t_1)^5(2e)^1$ and $(1t_1)^5(3t_2)^1$ respectively[286] These charge transfer

bands originate from π -type molecular orbital associated with the halogen to the metal d-orbitals (of eg and t_2g symmetry in octahedral nomenclature) similar assignments have been reported earlier.

The separation between first and second transitions is a measure of the ligand field parameter 10Dq. For chloride and bromide complexes it comes out to be in between $(8630 - 8700 cm^{-1})$ and $(5950 - 6200 cm^{-1})$ respectively and this quantity is seem to decrease in the order Cl $\sim$ Br.

Vo (IV) complex :

The analytical data indicate that the complex possess (1 : 1) compositions. The magnetic moment measured at room temperature is 1.76B.M., indicating monomeric nature of the complex and the absence of metal - metal interaction.

The assignments of electronic spectral bands of oxovanadium (IV) complexes have been a matter of controversy[287-290]. We have adopted here Ballhausen and Gray[291] scheme for assigning the transitions. The complex under study shows three transitions at 13710; 15360 and $24200 cm^{-1}$. The first band occurs as a broad band while the V_2 and V_3 as a weak bands. The single transition $2T_2 \longrightarrow 2E$ observed is a characteristic of vanadyl ion (Vo^{+2}) containing only one unpaired electron existing in the octahedral state. The values of ligand field parameters eg, Dq, DS and Dt have

Table - 7

Magnetic and electronic spectral studies of Ti (IV) and Oxovanadium (IV) complexes.

Complex	Band	Assignments	10 Dq	ueff
$[\text{Ti}(C_{17}H_{16}N_5O_2ClS)Cl_3]$ Cl. H_2O	32220	$(1t_1)^6 \rightarrow (1t_1)^5(2e)^1$	10730	1.66
	42950	$\rightarrow (1t_1)^5(3t_2)^1$		

$[\text{Vo}(C_{17}H_{16}N_5O_2ClS)]$ $(NCS)_2$ H_2O	Energy range cm^{-1}	B.G.(M.O) assignments	Transition in C_4V field	Transition in 'd' orbitals
Band I	11500 – 14500	$2B_2 \rightarrow 2E(V_1)$	$b_2 \rightarrow e \; x$	$xy \rightarrow xz, yz$
Band II	15000 – 18000	$\rightarrow 2B_1(V_2)$	$\rightarrow b_1$	$\rightarrow x^2 - y^2$
Band III	24000 – 29000	$\rightarrow 2A_1(V_3)$	$\rightarrow a_1$	$\rightarrow z^2$

ueff (1.76 B.M.)

been calculated using the equation - 3DS + 5Dt = 13710;
10Dq = 15360 and 10Dq - 4DS - 5Dt = 24200, which comes out
to be Dq (15360); DS (-3692) and Dt (856.8) respectively,
showing tetragonal distortion of the complex.

Infrared spectral studies :

An assignment of the important IR absorption bands
is based on the study of I.R. of free ligand and their
chelates and the same is reported in table (8). Complex
exhibit broad bands in the region 3200 - 3100 assignable
to -N - H-. The amide -C = O of the free ligand appear in
the region 1700 while in the complexes the v(C = O) occurs
in the region 1660 - 1680, this shows that the amides
C = O, takes part in complexation. The -N - C = S group
frequency was obtained at 1270cm^{-1}, also get shifted to
lower[292] side on chelation. Three bands around 840, 670
and 400 in the spectra of the complexes have been assigned
to the coordinated water molecule[293], and the last band
may also be due to metal oxygen bond.

Further it is worth while to examine the VCN
and VCS modes and the type of thiocynate bonding in the
vanadyl complex. For M- NCS bonding VCN and VCS fall in the
range 2080 - 2040cm^{-1} and 860-780cm^{-1} respectively. The
vanadyl complex show band around 2070cm^{-1} and 880cm^{-1} which
show that the thiocyanate group is linked to vanadyl ion
through N- bonded SCN group.

LT[[(C17 H16 N5 O2 Cl S)]Cl3 · H2O

Transmittance (%)

Wave number (cm⁻¹)

Fig.8

$[VO(C_{17}H_{16}N_5O_2ClS)(NCS)_2 \cdot H_2O]$
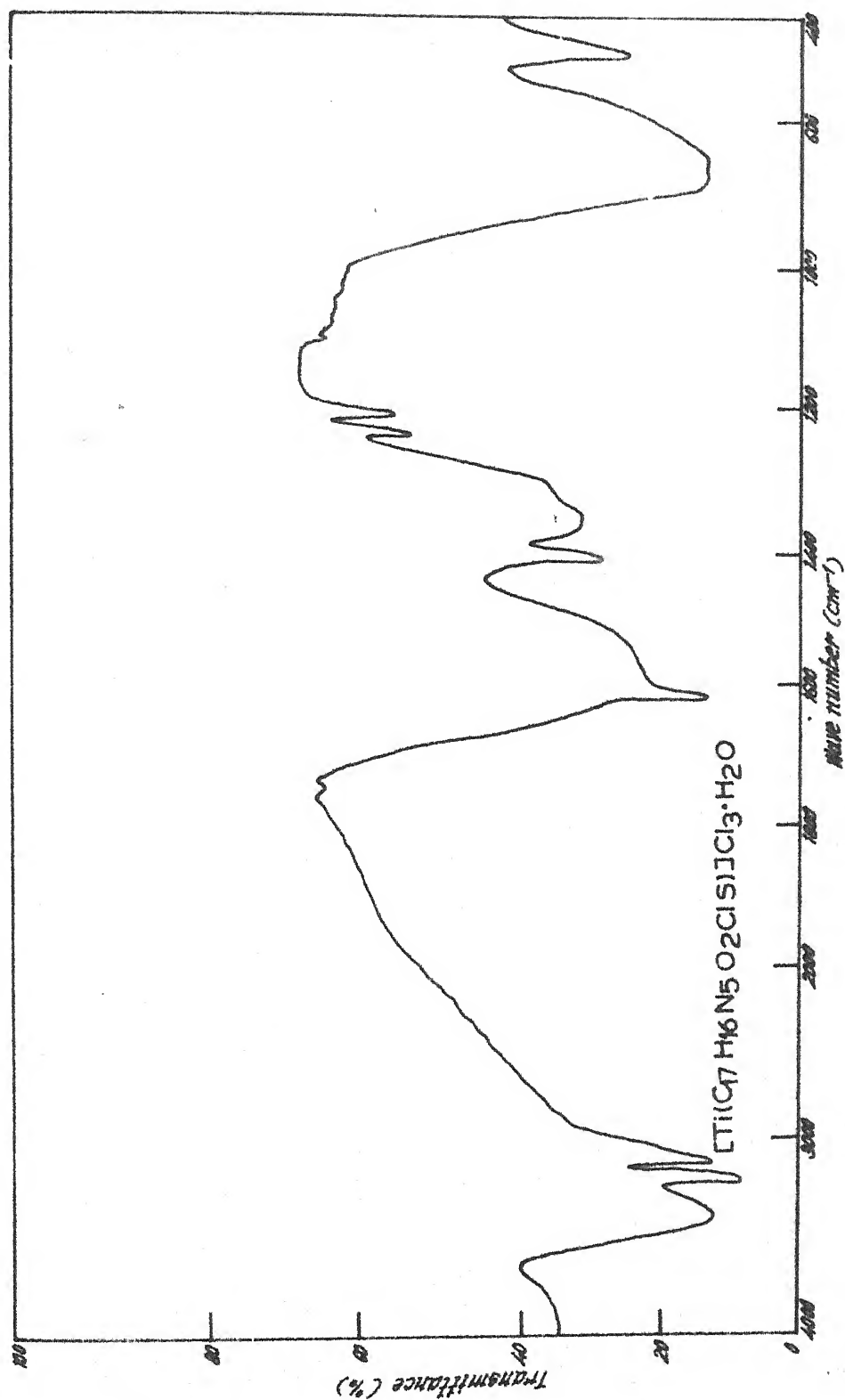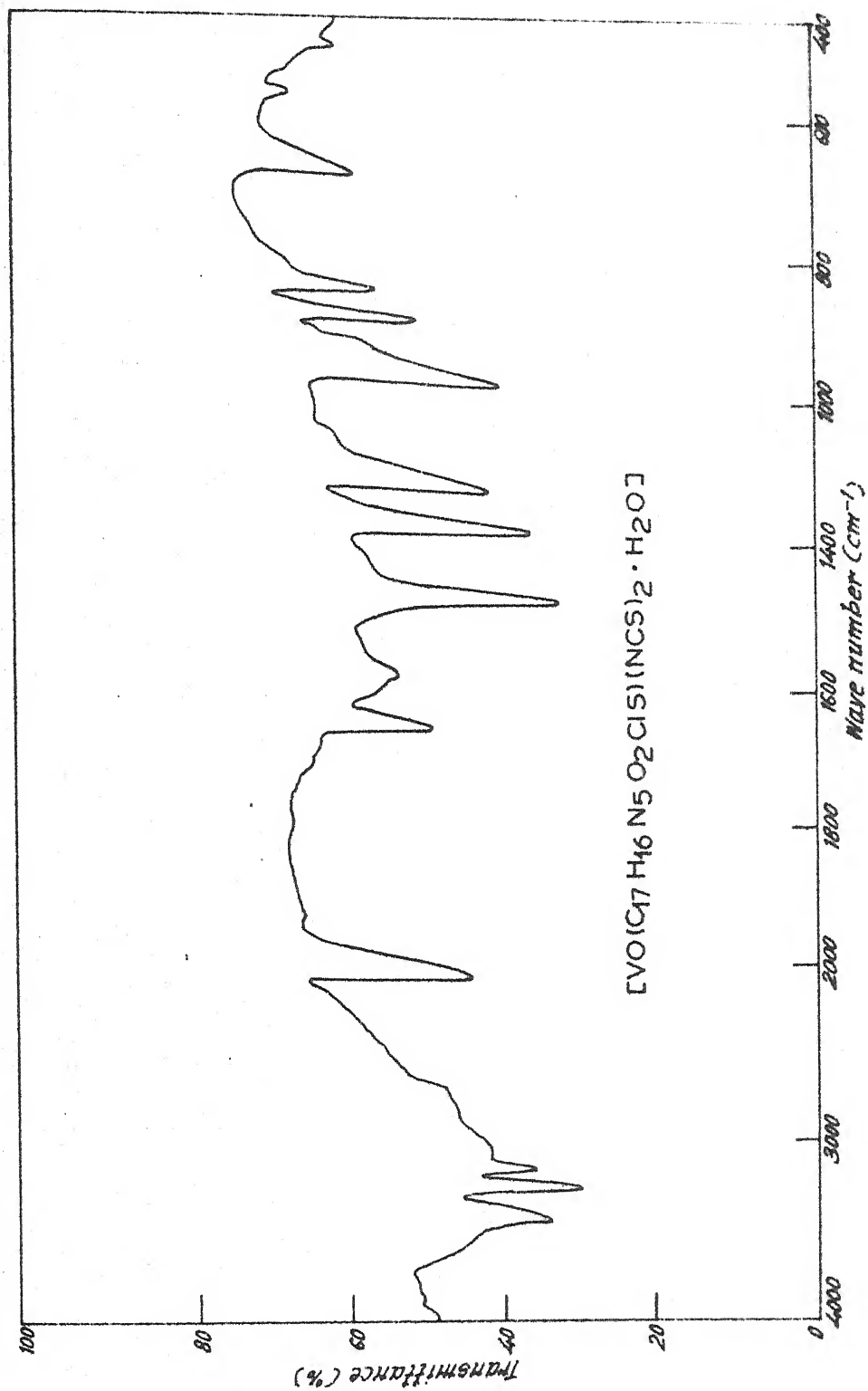
Fig.9

Table - 8

Selected IR absorption bands of Ti (IV) and Oxovanadium (IV)

complexes.

Thiosemicarbazide of of α-Benzamido-o-chlorocinnamic Acid	$\left[Ti(C_{17}H_{16}N_5O_2ClS)Cl \right] Cl_3.H_2O$	$\left[Vo(C_{17}H_{16}N_5O_2ClS)(NCS)_2 H_2O \right]$	Assignments
3200	3180	3160	-NH
1700	1680	1660	CONH
1280(S)	1250	1240	$\rangle C = S$
-	-	840, 870	$\delta(H_2O)$ coordinated
-	-	2070(S), 880(m)	NCS
-	1370(m)	1380 m(Sh)	$\nu(NH)$
-	3440	3460	$\nu(OH)$ of water
-	500(m)	980(m)	$r(M - O)$
3290(S), 1600(S)	3290(S), 1600(S)	3290(S), 1600(S)	-NHNH$_2$
1490(m)	1480(m)	1480(m)	$\delta CN + \delta NH_2 + CS$
Fig (A)	Fig (8)	Fig (9)	

Section – III

5-Acetyl-2-OH-Benzoic Acid thiosemicarbazide.

(A) Literature survey

(B) Preparation of 5-Acetyl-2-hydroxy benzoic acid
    thiosemicarbazide.

(C) Divalent metal complexes

   (i) Square planar complexes of copper (II) and
       palladium (II).

   (ii) Tetrahedral complex of cobalt (II)

   (iii) Octahedral complexes of trivalent metal ion
         chromium

   (iv) Oxovanadium (IV) complex

Section III – <u>Magnetic, electronic and spectral studies</u>
<u>of transition metal complexes of thiosemi-</u>
<u>carbazide of 5-Acetyl-2-OH-Benzoic Acid.</u>

<u>Literature survey</u> :

The thiosemicarbazide and its various thiosemi-
carbazones have been found to form tetragonally distorted
complexes with Cu (II)[294] and nickel (II)[295] ions.
Recently a reference to distorted octahedral complexes with
benzamido thiosemicarbazide[296] and its thiosemicarbazone[297]
has also been made, but no attempt have been made to
ascertain the nature of distortion, degree of distortion
and above all the causes of distortion. These studies
however, appear inconclusive in the absence of far infra red
spectral and low temperature magnetic measurements. A
considerable amount of work on transition and nontransition
metal complexes of acylhydrazones has been reported by
various workers[298-304]. However, little is known about
the complexing properties of acylthiohydrazides and thio-
hydrazone derivative though a number of Ni (II)- chelates
have been reported[305,306]. Numerous complexes of thio-
semicarbazide and thiosemicarbazones have been reported in
literature, not merely their use in analytical processes or
behaviour as pesticidal and fungicidal but also the activities
of such reagents[306-311] and some of their chelates find
tremendous use. Thiosemicarbazones form coordination[312-314]
polymers with bivalent ions. Some of its derivatives have
been tried for applications in medicine and a significant

correlation between the chelating properties and antitumour activity of a heterocyclic aldehydic thiosemicarbazones in animal systems has been noted. Special attention has been paid in the context of their activity against viruses, protozoa and small pox[315,316].

p-acetamidobenzaldehyde thiosemicarbazone is a well known antibubercular drug. Crim[317] and others have shown recently the importance of the metal chelates against cancer.

Recently orthohydroxy-4-benzamido thiosemicarbazide has been subjected to intensive studies[318]. The present work deals with the structure elucidation of some complexes of 5-acetyl-2-hydroxy benzoic acid thiosemicarbazide which were not reported earlier in literature. The ligand acts as a tridentate, bonding occuring through thioketo sulphur, amido nitrogen and phenolic oxygen.

Preparation of 5-acetyl-2-Hydroxy benzoic acid thiosemi-carbazide/detailed preparation.

(a) Preparation of acid hydrazide :

100 ml (1 M) of 5-acetyl-2-hydroxy methyl salicylate and 80 ml (1.5 M) of 99 percent hydrazine hydrate were refluxed on a water bath for about six hours. After cooling the acid hydrazide of the 5-acetyl-2-hydroxy methyl salicylate was obtained as a white crystalline solid.

(b) <u>Preparation of 5-acetyl-2-hydroxy-4-benzamido thiosemi-</u>
   <u>carbazide</u> :

The acid hydrazide (1 M) obtained in (a) was
suspended in 200 ml of liquor ammonia (density 0.88). 50 ml
of liquor ammonia, 45 ml of carbon disulphide (cooled to $0^{o}C$)
were added to the suspension of acid hydrazide in 15 ml
portions with constant stirring. The temperature was not
allowed to rise above $25^{o}C$ by external cooling. 100ml
of 95% ethanol were introduced and an additional 30 ml of
carbondisulphide followed by 100 ml of 95% ethanol were
added. The mixture was stirred for one hour by mechanical
stirrer. An aqueous solution of sodium monochloro
acetate (1 M), which was obtained by neutralisation of
(1 M) monochloroacetic acid with an equivalent amount of
sodium hydroxide, was added to the mixture when the solution
became warm due to an exothermic reaction. To this solution,
60ml (1.2 M) of 99% hydrazine hydrate were added when a
clear yellowish solution were obtained after stirring it for
half an hour. The mixture was concentrated on water bath
for three hours to half of its volume and cooled when a white
crystalline solid was separated out. The solid was recrysta-
llised from glacial acetic acid and dried.

Molecular formula - ($C_{10}H_{12}N_4O_3S$)   M.P ($112^{o}C$)

		C	H	N
Calculated %	–	44.78	4.48	20.9
Found %	–	43.17	4.26	20.9

The overall reaction may be represented as below :

$$\left[C_6H_3(OH)COCH_3.COOH \right] \xrightarrow[\text{Conc.}H_2SO_4]{CH_3OH} \left[C_6H_3(OH)COCH_3COOCH_3 \right]$$

$$\xrightarrow{H_2N.NH_2.H_2O} \left[C_6H_3(OH)COCH_3CONHNH_2 \right] \xrightarrow[\substack{\text{(ii) } CS_2 \\ \text{(iii) Ethanol}}]{\text{(i) } NH_3}$$

$$\left[C_6H_3(OH)COCH_3.CO.NHNH - \underset{\underset{S}{\|}}{C} - \overline{S} \; NH_4^+ \right] \xrightarrow{Cl.CH_2COONa}$$

$$\left[C_6H_3(OH)COCH_3.CONH.NHC.S.CH_2COONa \atop S \right] \xrightarrow{H_2N.NH_2.H_2O}$$

$$\left[C_6H_3(OH)COCH_3.CO.NH.\overset{4}{N}H.\overset{3}{\underset{\underset{S}{\|}}{C}}.\overset{2}{N}H.\overset{1}{N}H_2 \right]$$
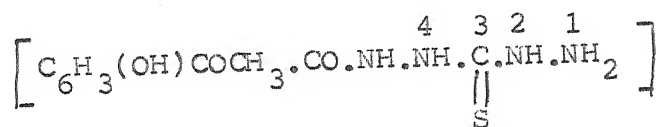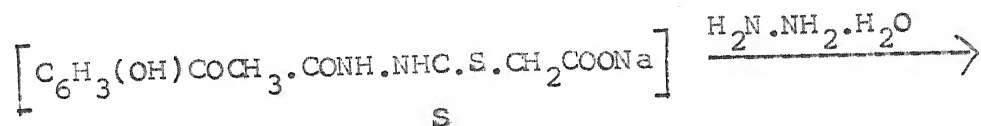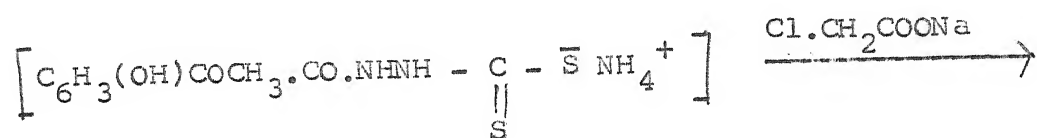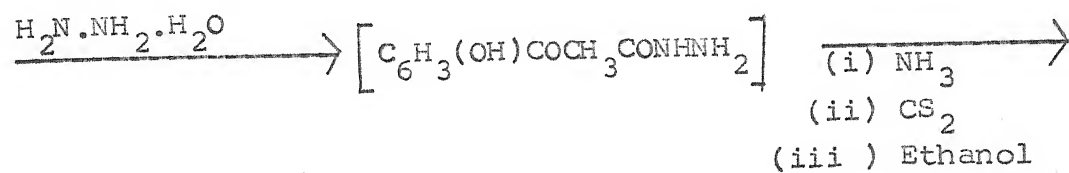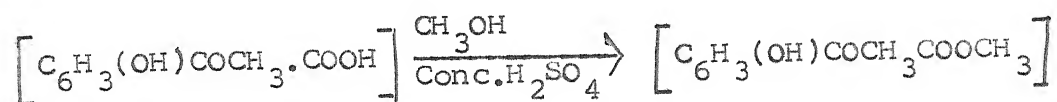
(c) - (i) <u>Octahedral complexes of manganese (II) and</u>

<u>nickel (II)</u>.

<u>Preparation of the complexes</u>

<u>Bis(5-acetyl-2-OH-benzoic acid thiosemicarbazide)</u>

<u>manganese (II)</u>.

30 ml of 0.05 M ethanolic solution of manganese (II) chloride tetrahydrate was mixed with 30 ml of 0.1 M solution of the ligand in the same solvent at pH$\sim$4.5. A light coloured precipitate was formed, it was refluxed for one hour, cooled and filtered off, washed with water and dried. Analysis correspond to $\left[Mn(C_{10}H_{11}N_4O_3S)_2 \right]$

	Mn	N	H
Calculated % —	9.33	19.02	3.74
Found % —	9.70	18.30	3.86

<u>Bis(5-acetyl-2-hydroxy benzoic acid thiosemicarbazide)</u> -

<u>nickel (II)</u> :

20ml of 0.5 M nickel (II) nitrate hexahydrate in ethanol was mixed with 40 ml of an equimolar ethanolic solution at pH 5. On refluxing the mixture brown coloured precipitate was obtained, it was filtered off, washed with water, dried and analysed.

$$\left[Ni(C_{10}H_{11}N_4O_3S)_2 \right]$$
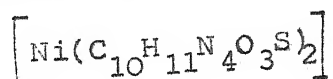
	Ni	N	H
Calculated % —	9.90	18.89	3.71
Found % —	10.24	18.40	3.56

The magnetic, electronic and spectral data of the isolated complexes have been recorded in table (9).

Results and discussion :

Manganese (II) ion has a d^5 configuration and is capable of forming spin free as well as spin paired complexes. Due to the additional stability of the half filled d-shell the spin free complexes are most predominent. The electronic ground state for manganese (II) ion is 6S and there is no angular orbital momentum even in the free ion, therefore, there will be no orbital contributions to the magnetic moment, which will be independent of the temperature and the stereochemistry[319,320]. The complex under study show magnetic moment value of 5.95 B.M. suggesting thereby that this is spin free complex having five unpaired electrons.

In Mn (II) complexes the intensity of the electronic transitions from the ground 6S to the states of four fold multiplicity are very weak and since Mn (II) has a d-five electronic configuration the same type of energy level diagram applies whether the metal ion is surrounded by tetrahedral or octahedral environment. Hexa aquamanganese (II), exhibits six electronic bands in two groups of three. In the present complex four bands have been observed which are assigned to the transitions $6A_1g \longrightarrow 4T_1g(4G).(10B + 5C);$

Table - 9

Magnetic and electronic spectral data of Mn (II) and Ni (II) complexes.

Complex compound	Bands	Assignment	B	C	F_2	F_4	Dq	β	hx
$[Mn(C_{10}H_{11}N_4O_3S)_2]$			539.28	3739	105	106.8	593.20	0.68	4.57
	32387	$6A_1g \longrightarrow 4T_1g(4P)$							
	27865	$6A_1g \longrightarrow 3Eg(4D)$							
	24090	$6A_1g \longrightarrow 4Eg, 4A_1g(4G)$							
	19853	$6A_1g \longrightarrow 4T_1g(4G)$							

ueff = 5.95 B.M.

			B	DS	Dt	DQ	DQZ^2
$[Ni(C_{10}H_{11}N_4O_3S)_2]$			1143	1442.13	395.42	1246	554
	9000	$3A_2g \longrightarrow 3T_2g(v_1)$					
	12460						
	16270	$3A_2 \longrightarrow 3T_1g(v_2)$					
	18660						

ueff = 3.20 B.M.

$$\frac{Dg}{B} = 1.09$$

$6A_1g \longrightarrow 4Eg \; 4A_1g(4G),(10B + 5C); \; 6A_1g \longrightarrow 4 \; Eg(4D)(17B + 5C)$ and $6A_1g \longrightarrow 4T_1g(4P)(7B + 7C)$. The values of ligand field parameter B and C have been calculated using the band $6A_1g \longrightarrow 4Eg \; 4A_1g(4G) \; (10B + 5C)$ and $6A_1g \longrightarrow 4Eg(4D)$ $(17B + 5C)$ which comes out to be 539.28 and 3739 respectively. These two transitions energies are independent of crystal field splitting energy and depends only on the parameters B and C. The value of Dq is obtained by the relationship $Dq/B = 1.1$. Slater condon shortly parameter F_2 and F_4 are related to Racah interelectronic repulsion parameters B and C as follow $B = F_2 - 5F_4$ and $C = 35F_4$. By using the values of Racah parameter B and C, values for parameter F_2 and F_4 have been calculated. The values of hx is obtained by using the relationship $(1 - \beta) = hx \; KM \; (KM = 0.07)$ and $B = 786$ for free Mn^{+2} ion. Kubelka - Munk remission function $F=(1-R)^2/2R$ was also calculated, where R is the optical density at a particular wave length.

Nickel (II) complex :

The magnetic moment observed for the present nickel (II) complex is 3.20 B.M. which is slightly higher than the spin only value of 2.83 B.M. for high spin octahedral complexes.

In general the ligand field spectra of octahedrally coordinated nickel (II) ions consist of three bands, the first band (V_1) assigned to the transition $3A_2g \longrightarrow 3T_2g$ $(7000 - 12000cm^{-1})$; the second band (V_2) $3A_2g \longrightarrow 3T_1g(F)$

($12000 - 20,000 cm^{-1}$) the third band (V_3) ($3A_2g \longrightarrow 3T_1g(P)$ ($21000 - 30,000 cm^{-1}$). Further more two spin forbidden transitions are sometimes found (V_4) in the region $11,500 - 15,500 cm^{-1}$ and V_5 in the region $17000 - 24000 cm^{-1}$.

The bands occuring at 9000; 12460; 16270 and 18660 suggesting octahedral structure for the complex. These bands may be assigned to $3A_2g \longrightarrow 3T_2g$($V_1$ 9000 and 12460) and $3A_2g \longrightarrow 3T_1g$ (V_2, 16270 and 18660). The probable assignments for split components in D_4h can be given as $3B_1g \longrightarrow 3Eg(9000)$, $3B_1g \longrightarrow 3B_2g(12460)$, $3B_1g \longrightarrow 3A_2g$ (16270) and $3B_1g \longrightarrow 3Eg(F)$ (18660).

The amount of splitting in V_1 is a measure of degree of distortion (12460 - 9000 = 35/4 Dt). From this Dt comes out to be 395.42, similarly, the amount of splitting of V_2 band is expected to the extent of (2Ds-5/4 Dt), by substituting the value of Dt, Ds comes out to be (1442.13) eg V_2 (18660 - 16270) = 2DD - 5/4 Dt.

Now Dt (D_4h) = $\frac{4}{7}$ ($Dq^{xy} - Dq^{z^2}$) and

Dq^{xy} = 1246, the value of Dq^{z^2} (554) has been calculated.

The ratio of V_2/V_1 (18660/9000)(2.07) found to be greater than that required for octahedral structure showing considerable distortion from the cubic field. From the above discussion it may be concluded that the field in xy plane is stronger than that along the z- axis.

The spin orbit coupling constant ($-\lambda$) has been

calculated from the spectral parameters using the equation
$-\lambda = 0.27 \ B^2/Dq$ which comes out to be $283 cm^{-1}$ in close
agreement with the reported data.

Infrared studies :

The spectra of both ligand and the complexes
show strong absorption bands near 3550 and 3440 dut to
phenolic -OH and (N-H) stretching vibration. The bands
at 1680 and $1350 cm^{-1}$ are due to (CONH) and (C = S)
respectively. The complexes show no absorption at the
higher wave number region indicating the formation of a
bond between metal and phenolic oxygen by loss of a proton
from the phenolic group.

There occur change in the frequency of the
observed (C = S) stretching vibrations and this may be
taken as evidence for sulphur participation in complexes.
A comparison of the position of the amide I band in the
ligand and the Mn^{+2} and Ni^{+2} complexes suggest that the
oxygen coordination may be excluded. The change exhibit by
δ NCO on complex formation indicate the involvement of the
amide nitrogen[321] atom.

Thus the IR studies suggest that the coordination
of the ligand to the metal through the thio-ketosulphur,
amido nitrogen atoms and the phenolic oxygen, hence making
the ligand a tridentate one.

The above spectral and magnetic study suggests
the distorted octahedral symmetry of the complexes under
study.
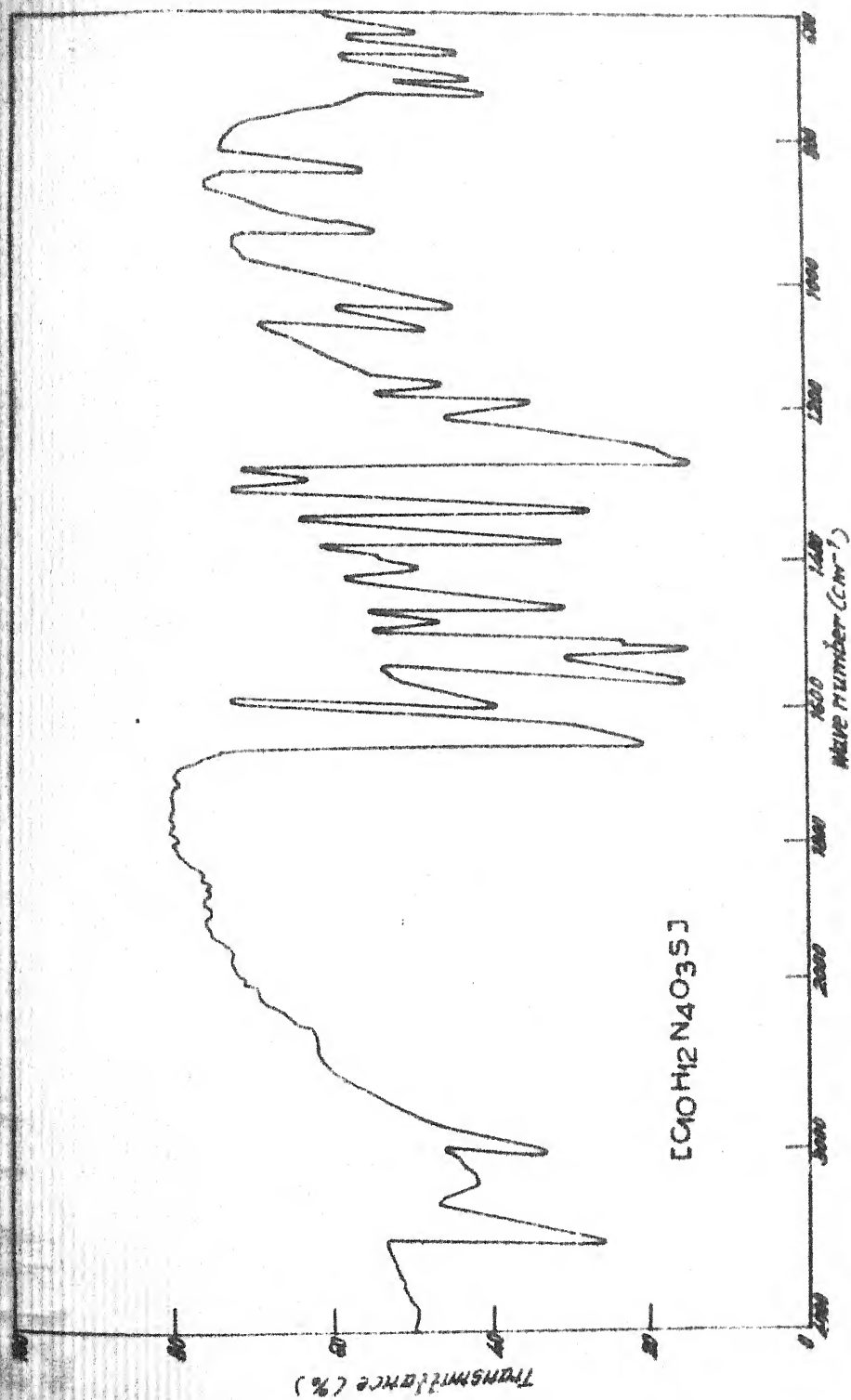
[C₁₀H₁₂N₄O₃S]

Fig 10 - I.R.Spectra of thio semicarbazide of 5-acetyl-2-hydroxybenzoic acid.

$[Mn(C_{10}H_{11}N_4O_3S)_2]$

Fig.11

[Ni(C₁₀H₁₁N₄O₃S)₂]

Wave number (cm⁻¹)

Transmittance (%)
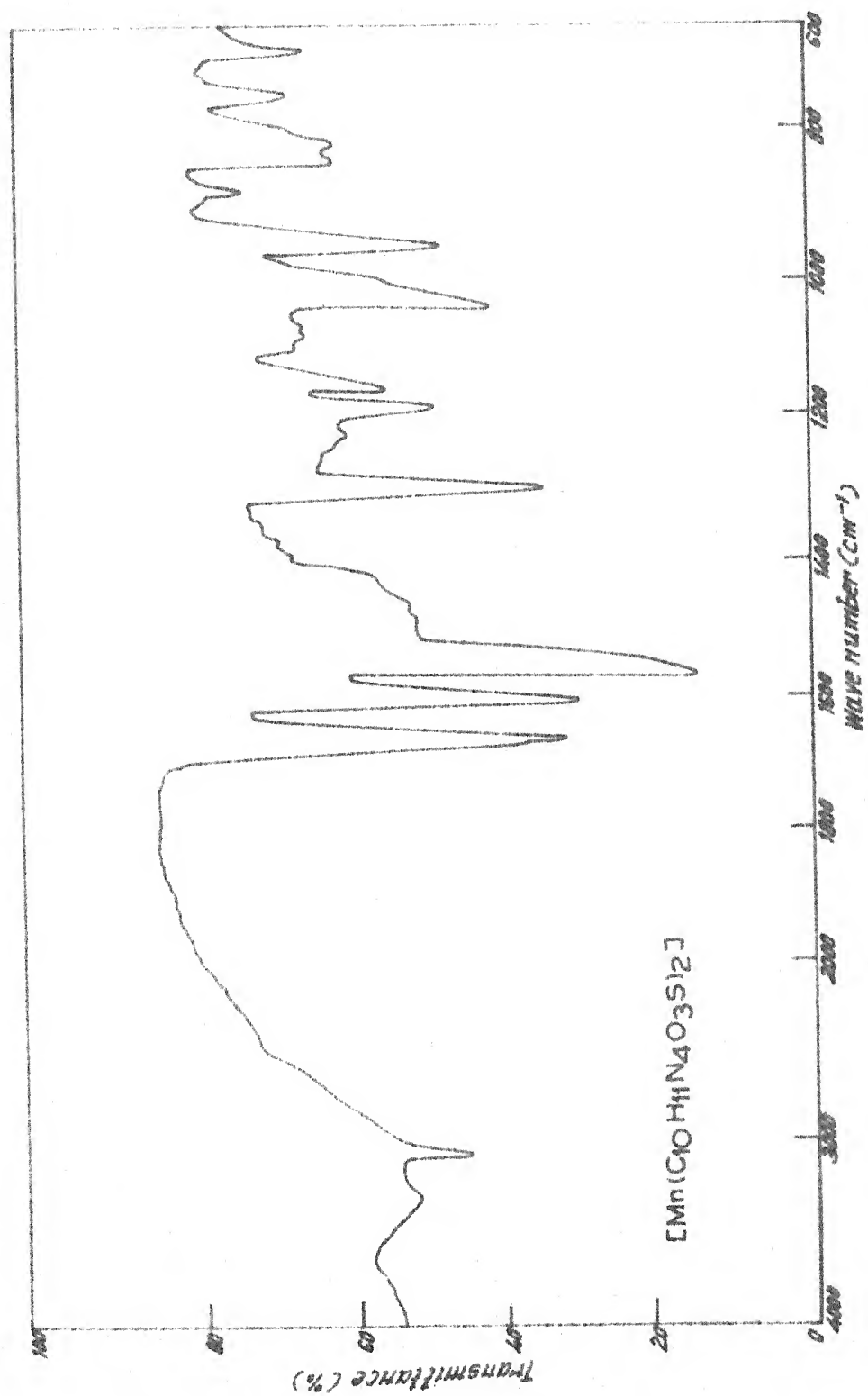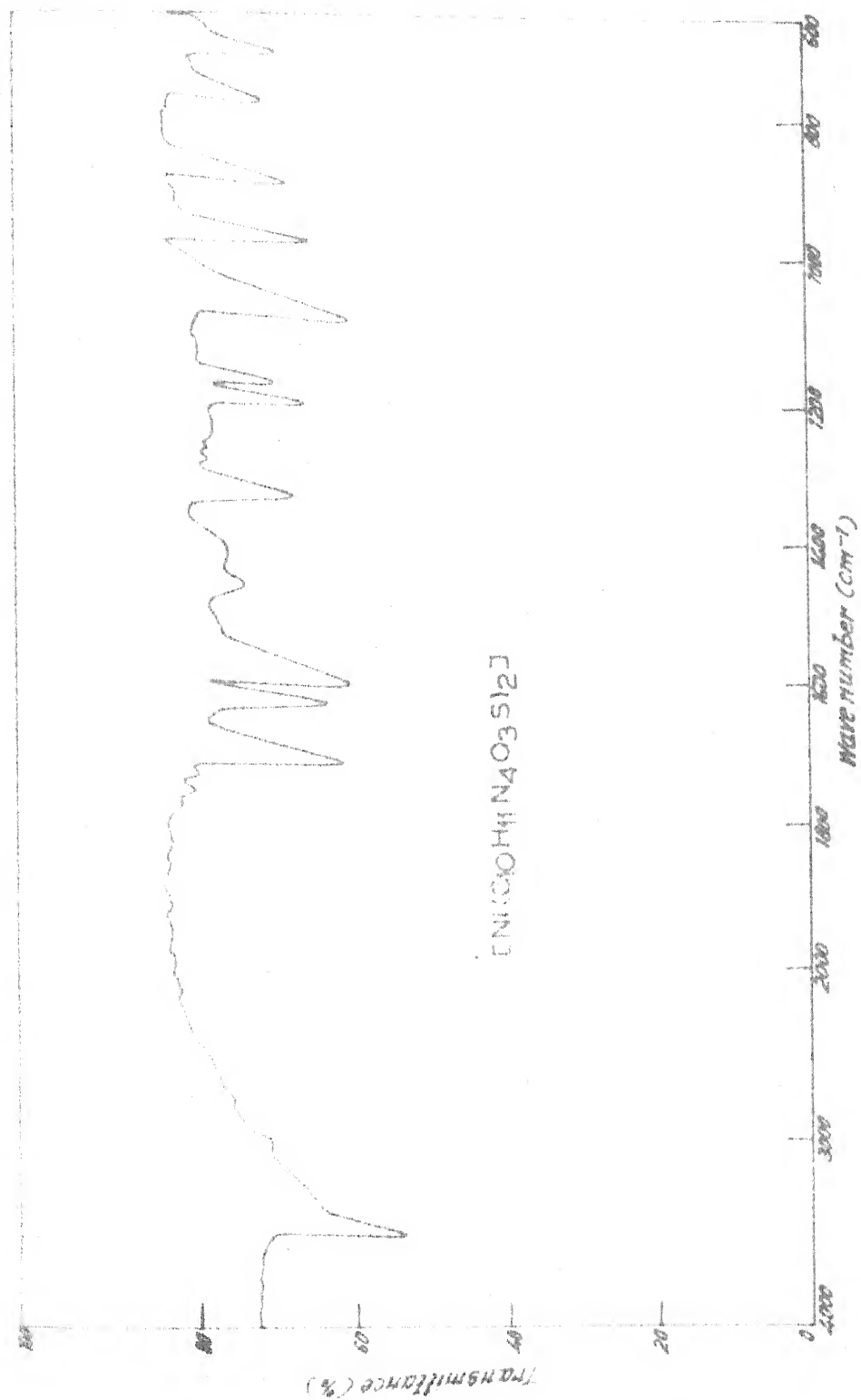
Fig.12

Table - 10

Infrared spectral measurement of Mn^{+2} and Ni^{+2} complexes of thiosemicarbazide of

5-acetyl-2-OH-Benzoic Acid.

(5 - AHBT) $(C_{10}H_{12}N_4O_3S)$	$[Mn(C_{10}H_{11}N_4O_3S)_2]$	$[Ni(C_{10}H_{11}N_4O_3S)_2]$	Assignments
3545(S)	—	—	r(O–H) of Phenol
1680(m)	1670(Vs)	1700	r(CONH)
3040(m)	3040(m)	3040(m)	r(C – H)
1350	1310	1320	r(C = S)
960(S)	960(S)	960(S)	–CH out of plane bending
1630	1620(S)	1620(S)	Amide I + NH bend
1590(S)	1580(w)	1590(m)	NH bend
1190(w) 1170(m) 1060(w)	1190(w) 1160(m) 1070(w)	1190(w) 1160(m) 1070(w)	CN –stretch and CS band (amide II)
870(w)	880(w)	880(w)	NH– stretch
760(w)	750(w)	760(w)	δNCO
700(m)	690(m)	700(m)	NH out of plane
Fig (10)	Fig (11)	Fig (12)	

(ii) <u>Square planar complexes of Cu (II) and Pd (II)</u>.

<u>Preparation of the complexes</u> :

To the metal solution in 25 ml ethanol 0.42g of $\left[Cu(CH_3COO)_2.H_2O\right]$ or 0.40g of palladium chloride, 0.50g of thiosemicarbazide of 5-acetyl-2-hydroxy benzoic acid was added with constant stirring, after raising the pH $\sim$ 8.0. The mixture when refluxed for about one hour and left overnight yielded the complex, which was filtered, washed with water, and dried over calcium chloride in a vacuum desicator. The chemical analysis correspond to $\left[Cu(C_{10}H_{11}N_4O_3S)(OH)\right]$ and $\left[Pd(C_{10}H_{11}N_4O_3S)(OH)\right]$
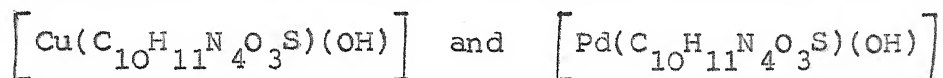
	Calculated %	Found %
Cu -	18.28	18.70
N -	16.11	16.72
Pd -	27.25	26.56
N -	14.34	13.90

The magnetic, electronic spectral and other parameters are given in table (11).

<u>Results and discussion</u> :

Copper (II) display magnetic moment value in the range 1.80 - 1.90 B.M. similar to magnetically dilute copper (II) complexes[322,323], whereas for tetrahedral configuration the moments will be larger than 2.0 B.M.

Table – 11

Magnetic moment, Electronic spectra and other parameters.

Complex	Position of bands cm^{-1}	Assignments	$\triangle_1\ cm^{-1}$	$\triangle_2\ cm^{-1}$	$\triangle_3\ cm^{-1}$	Magnetic moment (B.M)
$[Cu(C_{10}H_{11}N_4O_3S)(OH)]$	24000	$2B_1g \longrightarrow 2A_1g$	–	–	–	1.75
	13000	$2B_1g \longrightarrow 2Eg$				
$[Pd(C_{10}H_{11}N_4O_3S)(OH)]$	15380	$1A_1g \longrightarrow 1A_2g$	18880	4000	11030	Diamagnetic
	17880	$\longrightarrow 1E_1g$				
	28410	$\longrightarrow 1B_1g$				

1 B.M. = $9.273 \times 10^{-24} Am^2$.

In the present case magnetic moment value of the complex suggest square planar structure.

Though three transitions $2B_1g \longrightarrow 2A_1g$, $2B_1g \longrightarrow 2B_2g$ and $2B_1g \longrightarrow 2Eg$ are expected for copper (II) complexes, since they are very close in energy hence often give rise one broad band envelop. Sacconi[324] and Meek[325] and Ehrhardt have observed that square planar complexes have a complex broad band at relatively higher frequencies $(16,000 \text{cm}^{-1})$. The regular tetrahedral complexes of copper(II) show no (d-d) absorption bands in the region[326] $10,000 - 20,000 \text{cm}^{-1}$. The spectra show two strong but broad bands at around 24000 and 13000cm^{-1}, which is similar to other planar complexes[327-330] of copper (II), and the two bands may be assigned to $2B_1g \longrightarrow 2A_1g$ and $2B_1g \longrightarrow 2Eg$ transitions respectively in D_4h symmetry.

Palladium (II) complex :

The magnetic measurement reveals the diamagnetic nature of the palladium (II) complex. The tendency of nd^8 metal ions to form square planar complexes increases in the order of Ni (II)   Pd(II)   Pt(II).

The ground state for the d^8 low spin $(Pd \; X_4)^{+2}$ is $\left[ag(Z^2)\right]^2 \left[eg(xz,yz)\right]^4 \left[b_2g(xy)\right]^2 \equiv 1A_1g$. Ligand field excited states are $^{3,1}A_2g(b_2g \longrightarrow b_1g)$, $^{3,1}Eg(eg \longrightarrow b_1g)$ $^{3,1}B_1g(a_1g \longrightarrow b_1g)$. The three electronic spectral bands observed at 15380, 17880 and 28410 may be assigned to the

transitions $1A_1g \longrightarrow 1A_2g \left[b_2g \; (\frac{X}{\pi}) \longrightarrow b_1g \; (\frac{X}{\sigma}) \right]$,

$1A_1g \longrightarrow 1E_1g \left[eg \; (\frac{X}{\pi}) \longrightarrow b_1g(\frac{X}{\sigma}) \right]$ and $1A_1g \longrightarrow 1B_1g$

$\left[a_1g(\frac{X}{\sigma}) \longrightarrow b_1g \; (\frac{X}{\sigma}) \right]$ respectively. Since electronic

excitations into the virtual orbital b_1g lead to states to

the following symmetries and energies[331] relative to the

ground state

$$b_2g \longrightarrow b_1g \qquad 1A_2g, \qquad W = \triangle_1 - C$$

$$eg \longrightarrow b_1g \qquad 1Eg, \qquad W = \triangle_1 + \triangle_2 - (3B + C)$$

$$a_1g \longrightarrow b_1g \qquad 1B_1g, \qquad W = \triangle_1 + \triangle_2 + \triangle_3 - (4B + C)$$

where B and C are Racah parameters and their values have been

taken as 500 and 3500cm^{-1} respectively. The values of

ligand field parameters $\triangle_1$, $\triangle_2$ and $\triangle_3$ have been evaluated

to be 18880, 4000 and 11030cm^{-1}. respectively. The higher

value of $\triangle_1$ is due to relative energies of the $b_1g(x^2 - y^2) \frac{X}{\sigma}$

and $b_2g(xy) \frac{X}{\pi}$ levels and therefore both σ and π bonding

are contributing factors.

Infrared spectra :

The i, r spectrum of the thiosemicarbazide

shows a weak band at 3545cm^{-1} which is assigned to hydrogen

bonded O - H stretching of phenolic group. This band disappear

in the spectra of complexes indicating the involvement of

phenolic OH in complexation. The band at 1680cm^{-1} assigned

as the amide I band is shifted to a lower frequency by 10-20cm^{-1}

[Cu(C$_{10}$H$_{11}$N$_4$O$_3$)(OH)]

Wave number (cm^{-1})

Transmittance (%)

Fig.13
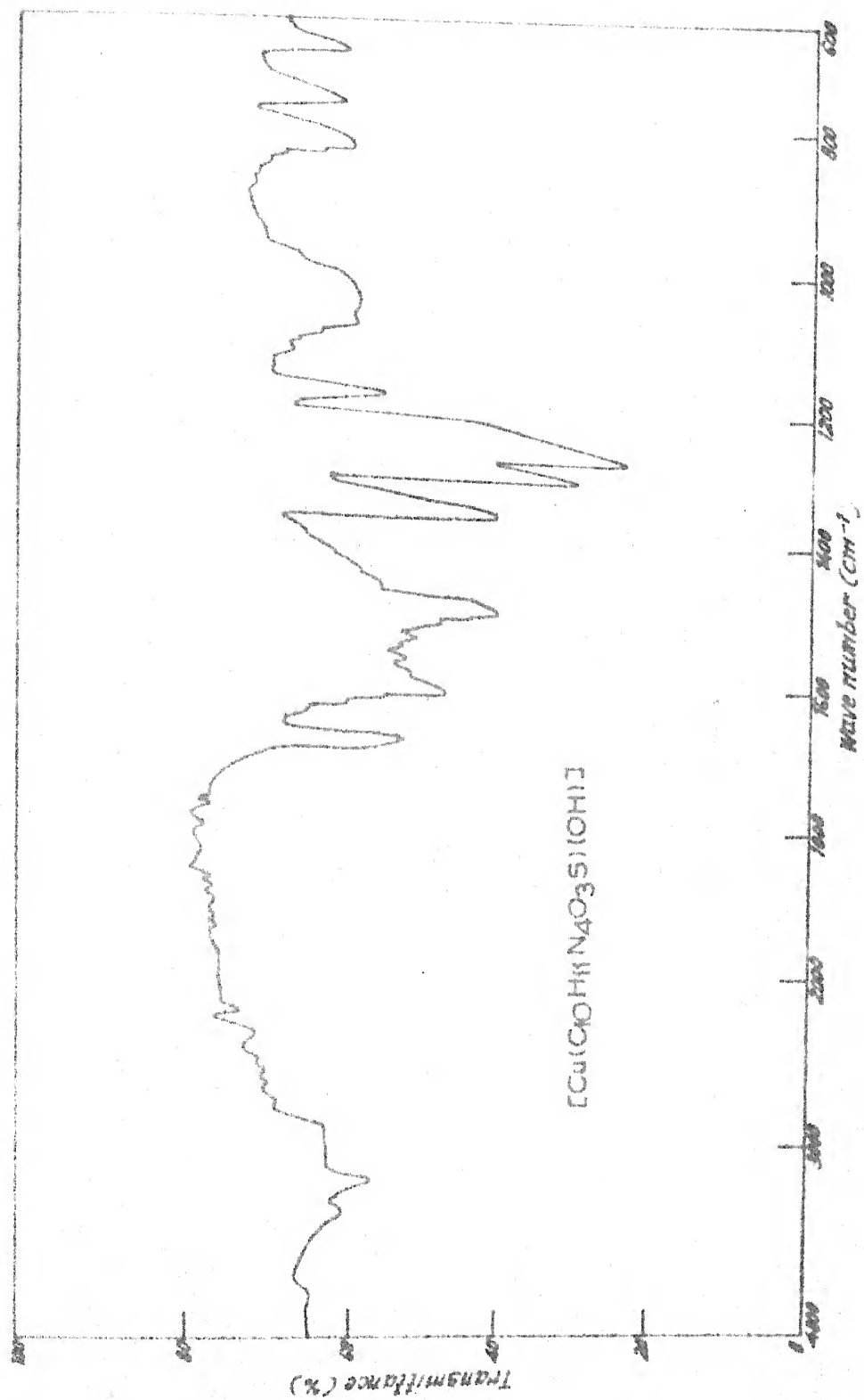
[Pd(C$_{10}$H$_{11}$N$_4$O$_3$S)(OH)$_2$Pd]
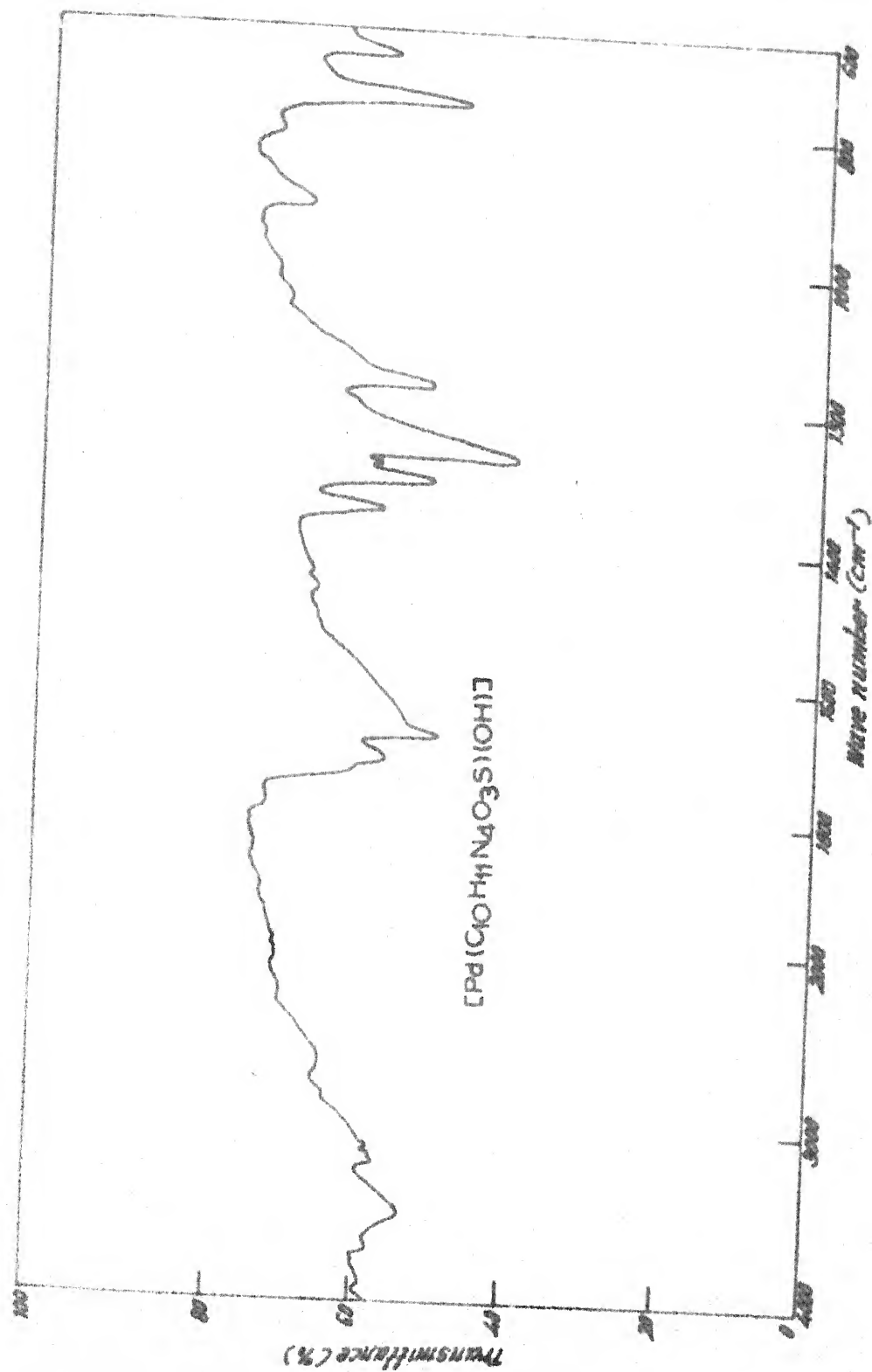
Fig.14

Table - 12

Infrared spectral bands and their assignments.

(5-AHBT) $(C_{10}H_{12}N_4O_3S)$	$[Cu(C_{10}H_{11}N_4O_3S)(OH)]$	$[Pd(C_{10}H_{11}N_4O_3S)(OH)]$	Assignments
3545(S)	–	–	Phenolic OH
1680(S)	1670(m)	1665(m)	-CONH
1350(S)	1340(S)	1340(S)	(C = S)
1280(m)	1290(m)	1300(m)	CS stretch, CN-stretch
1260(m)	1260(m)	1280(m)	
1170(m)	1168(m)	1160	NCS band
750(m)	750(m)	760(m)	δNCO, CS and CN stretch
680(m)	694(m)	680(w)	NH out of plane deform
Fig (10)	Fig (13)	Fig (14)	

in the Cu^{+2} and Pd^{+2} complexes indicating the participation of the amido nitrogen in coordination. The $(C = S)$ frequency at $1350 cm^{-1}$ in the free ligand is also found to be shifted to a lower frequency by $5-10 cm^{-1}$ in the complexes suggesting its involvement in coordination.

(iii) Tetrahedral complex of Cobalt (II)

Preparation of the complex

Monohydroxo mono(O-ASC) Cobalt (II) Dihydrate :

An ethanolic solution of cobalt (II) chloride hexahydrate was added to the thiosemicarbazide of 5-acetyl-2-hydroxy benzoic acid dissolved in ethanol. The resulting solution was refluxed on a steam bath for about half an hour, when a coloured solid was precipitate out. The product was filtered, washed with water and dried at 120°C.

The analytical results are in good agreement of the suggested formula $\left[Co(C_{10}H_{11}N_4O_3S)(OH)\right]2H_2O$

	Co	N
Calculated % —	11.55	14.78
Found % —	15.90	14.22

Results and discussion :

The complex shows 1:1 metal to ligand stoichiometry. Magnetic moment (4.40 B.M) of the complex indicate a tetrahedral configuration.

In a field of tetrahedral symmetry the 4F ground state of Co^{+2} is split into $4A_2$, $4T_2$ and $4T_1(F)$. The transitions $4A_2 \longrightarrow 4T_2$, $4A_2 \longrightarrow 4T_1(F)$, and $4A_2 \longrightarrow 4T_1(P)$ are designated as V_1, V_2 and V_3 respectively. The following

relationships are used to calculate $\triangle$ and B.

$$V_1 = \triangle \qquad \text{----- (1)}$$
$$V_2 = 1.5\triangle + 7.5B^1 - Q \qquad \text{------ (2)}$$
$$V_3 = 1.5\triangle + 7.5B^1 + Q \qquad \text{------ (3)}$$
$$Q = \frac{1}{2}\left[(0.6\triangle - 15B^1)^2 + 0.64\triangle^2\right]^{\frac{1}{2}} \text{ -- (4)}$$

The above equation on solving produces

$$\triangle = \frac{V_2 + V_3 - 15B^1}{3} \qquad \text{------ (5)}$$

$$Q = \frac{1}{2}(V_3 - V_2) \qquad \text{----- (6)}$$

and $4Q^2 = \triangle^2 - 18B^1\triangle + 225(B^1)^2$ $\qquad$ ----- (7)

The complex shows two transitions at 7400(V_2) and 16750 (V_3) assignable to $4A_2 \longrightarrow 4T_1(F)$ and $4A_2 \longrightarrow 4T_1(P)$ respectively substituting, the values of V_2 and V_3, Q and $\triangle$ comes out to be 4675 and $\triangle = 5(1610 - B^1)$ respectively, which gives the value of $B^1 = 398$.

Infrared spectra :

The assignments of the absorption bands observed for the Co^{+2} - thiosemicarbazide adducts are as follows. The bands in the region 1680, 1350 and $3545cm^{-1}$ are assignable to -CONH, C = S and pehnolic -OH on chelation the absorption frequency of -CONH and (C = S) decreases where as that of phenolic -OH disappears. This indicate that these are the coordinating sites.

The band in the region $3300-3480cm^{-1}$ and $1600cm^{-1}$ in the complex may be due to (OH) group of the water molecule.

Table – 13

Magnetic and spectral data of Co^{+2} complex.

Compound	Observed bands cm^{-1}	Assignments	10Dq	Racah parameter (B)	B.M.
$[Co(C_{10}H_{11}N_4O_3S)(OH)]\,2H_2O$	5000	$^4A_2 \longrightarrow {}^4T_1(F)(V_2)$	5000	398	4.40
	7400				
	16750	$^4A_2 \longrightarrow {}^4T_1(P)(V_3)$			

$[Co(C_{10}H_{11}N_4O_3S)(OH)_2]\cdot 2H_2O$

Wave number (cm^{-1})

Transmittance (%)
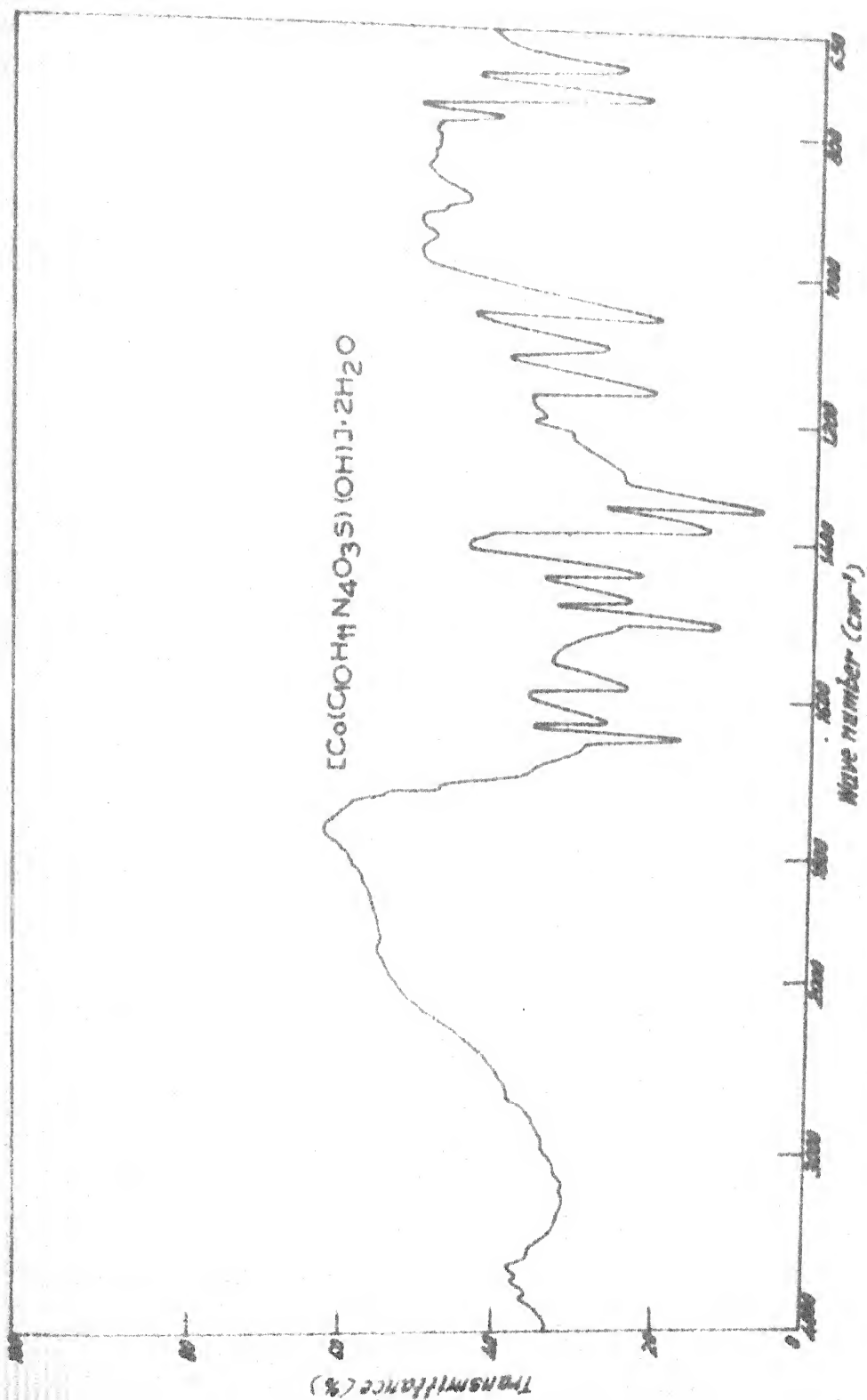
Fig. 15

Table - 14

Infrared absorption bands of thiosemicarbazide complex of cobalt (II) in cm^{-1}.

Thiosemicarbazide of 5-Ac-2-OH-Benzoic Acid	$[Co(C_{10}H_{11}N_4O_3S)(OH)]$ $2H_2O$	Assignments
3545	–	–OH
1680	1660	–CONH
1350	1330	–C = S
1630(s)	1625(s)	Amide I + NH bend
1590(s)	1580(s)	NH– bend
1500(s)	1490(s)	
1430(m)	1460(s)	CH– bending
1400(s)	1420(s)	
1380(m)	1360(m)	
1160(m)	1160(m)	CN stretch and CS bend
1075(w)	1100(m)	amide (III)
1050(w)	1060(m)	(CO)
760(m)	770(m)	δNCO, CS and CN stretch
750(m)	740(m)	NH out of plane deformation
700(m)	690(m)	
Fig (10)	Fig (15)	

Trivalent metal complexes

Dihydroxo mono (5-Ac-2-OH- Benzoic acid thiosemicarbazide chromium (III) :

An ethanolic solution of chromium chloride was added to the ligand (1 : 1 molar proportion) dissolved in ethanol. The pH of the solution was adjusted to ⌣10 by adding ammonium hydroxide solution. From the resulting solution brownish coloured precipitate was obtained. The product was filtered washed with alcohol and dried in vacuo over calcium chloride.

Analysis correspond to the formula

$$\left[Cr(C_{10}H_{11}N_4O_3S)(OH)_2(H_2O) \right]$$
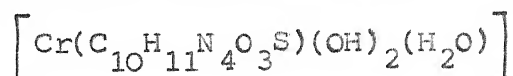
	Cr	H	N
Calculated % -	14.01	4.04	15.09
Found % -	14.56	4.20	14.70

Results and discussion :

Magnetic moments observed for the present complex is 3.80 B.M which is slightly less from the spin only value and may be a consequence of positive spin orbit coupling constant and magnetic anisotropy irrespective of the nature of the bond involved. The spectrum of the complex exhibits bands at 11970 and 18300 and a shoulder at 33540 may be assigned to $4T_2g \leftarrow 4A_2g(V_1)$ and $4T_1g \leftarrow 4A_2g(V_2)$ transitions respectively for a octahedral complex. The weak

Table – 15

Magnetic electronic spectral and relevant ligand field parameters of chromium (III) complex.

Complex	Observed bands cm^{-1}	Assignments	10Dq cm^{-1}	Racah parameter (cm^{-1}) meter B_{35}	B_{35}	Nephelauxetic ratio β_{35}	β_{35}	L.F.S.E K.Cals/mole
$[Cr(C_{10}H_{11}N_4O_3S)(OH)_2(H_2O)]^+$	13000	$4A_{2}g \rightarrow 4T_{2}g(F)(v_1)$	13000	918	546	0.93	0.59	44.57
$ueff = 3.80$ B.M.	18300	$4A_{2}g \rightarrow 4T_{1}g(F)(v_2)$						
	33540	$4A_{2}g \rightarrow 4T_{1}g(P)(v_3)$						
	9800	$4A_{2}g \rightarrow 2Eg$						

$Dt = 1485.71;$ $DS = 3578;$ $DqA = 1299$

Table - 16

Infrared spectral band assignments of Cr^{+3} complex.

(5 - AHBT)	$\left[Cr(C_{10}H_{11}N_4O_3S)(OH)_2(H_2O)\right]$	Assignments
3545(S)	-	Phenolic OH
1680(S)	1660(m)	CONH
1350	1330(m)	(C = S)
-	3000(m)	V(OH) of water
1630(m)	1635(S)	Amide I + NH bend
-	900(w) 930(m)	$\delta r(H_2O)$ coordinated
700(m)	690(s)	NH out of plane
Fig (10)	Fig (16)	

band at 9800 may be spin forbidden in nature corresponding to $4A_2g \longrightarrow 2Eg$ transition. The value of B_{35} has been determined by fitting the second (V_2) and third (V_3) bands

as $\qquad B_{35} = \dfrac{V_2 + V_3 - 3V_1}{15}$ which comes out to be 918 and B_{35} has been obtained using $E(2Eg \longleftarrow 4A_2g) = 9B_{35} + 3C - 5 (B_{35}^2/Dq)$ assuming $C = 4B$ and the value of B_{55} comes out to be 546. The value of β_{55} has been evaluated to 0.59 and the covalency parameter $1 - \xi = \dfrac{\beta_{35}}{\beta_{55}} = 1.57$. The energies of the (d-d) orbitals in terms of tetragonal radial parameters (Dt and DS) have been evaluated by the fact that the splitting of the first excited terms $1T_1g$ in octahedral symmetry is $35/4$ Dt and the parameter 10DqE corresponds exactly to 10DQ, DQ^A and DS have been determined using the equation.

$$Dt (D_4h) = \frac{4}{7} (Dq^E - Dq^A) \text{ and}$$
$$(V_2 - V_1) = 2DS - 5/4Dt$$

Infra red spectra :

The medium strong band at $3545 cm^{-1}$ in the free ligand may be assigned to the phenolic group of the molecule. The complex does not show this frequency in this region indicating the involvement of phenolic oxygen in coordination by a loss of proton.

$[Cr(C_{10}H_{11}N_4O_3S)(OH)_2(H_2O)]$
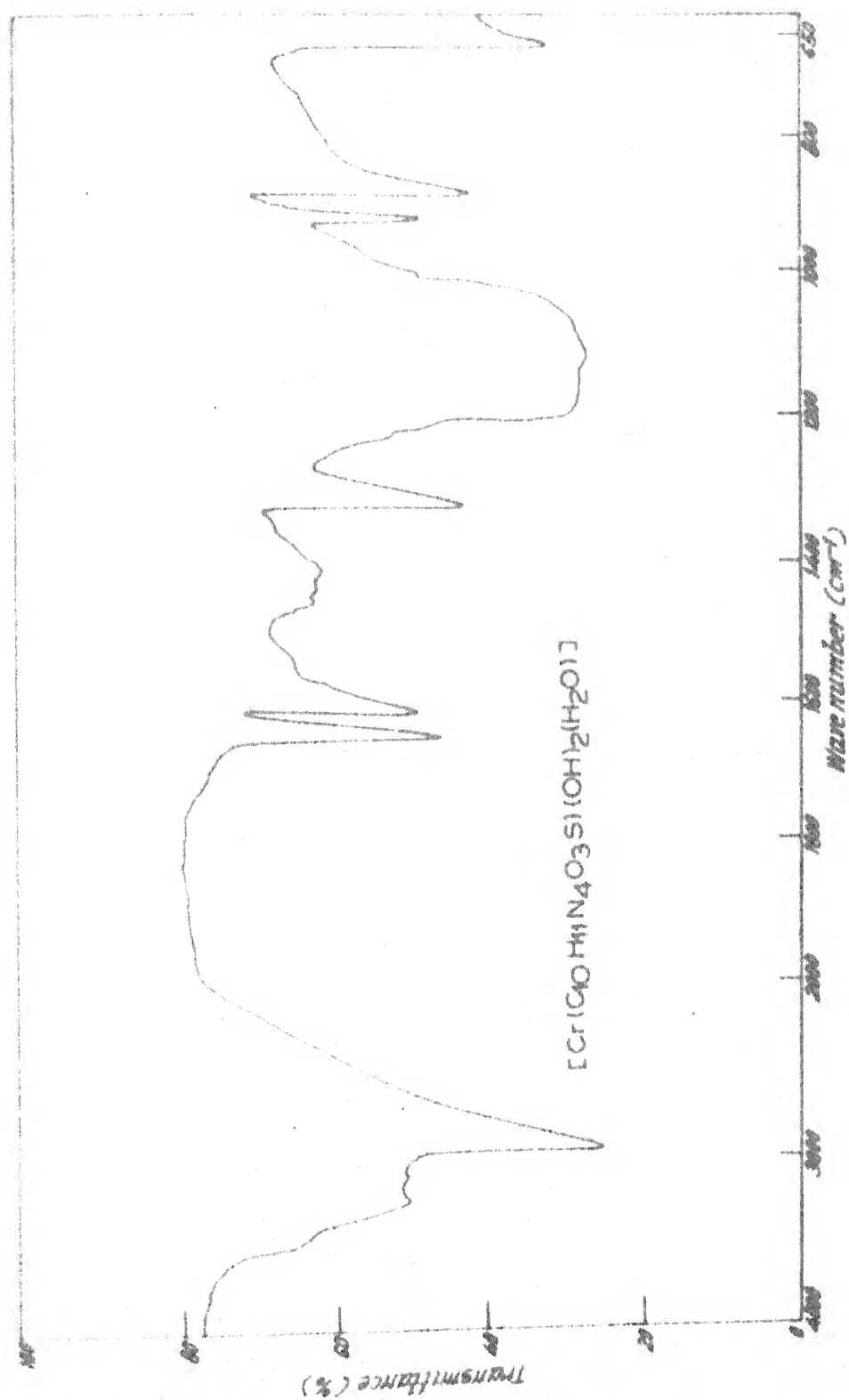
Fig. 16

The frequencies at 1680 and $1350cm^{-1}$ are assigned to amido and thione group, which get decreased considerably.

The vibrations appearing at $\sim 3000cm^{-1}$ and $900cm^{-1}$ may be assigned to the presence of OH group and water molecule in the complex.

Oxovanadium (IV) complex :

Ethanolic solution of oxovanadium (IV) chloride (0.05 m) was added to the thiosemicarbazide solution (0.05 mole) in the same solvent. The resulting mixture was refluxed for two hour on a water bath. The separated product was suction filtered, washed thoroughly with distilled water and dried in oven at $100^{O}C$. Analysis corresponds to the formula $\left[Vo(C_{10}H_{11}N_4O_3S)(H_2O)_2 \right] Cl$

		V	N	H
Calculated %	–	12.56	13.81	3.70
Found %	–	12.98	13.27	3.86

Results and discussion :

The analytical data of the complex indicate 1-1 (ligand-metal) stoichiometry and hence the ligand behaves as a tridentate monobasic ligand in the present complex. The complex possess 1.8 B.M. magnetic moment which is close to the spin only value of 1.73 B.M. expected for the $3d^1$ complexes when the orbital contribution is a completely quenched[332].

The electronic spectrum of the complex shows three bands around 12532; 17107 and 25460cm^{-1} which are assigned to dxy $\rightarrow$ dxz, dyz; dxy $\rightarrow$ dx^2 - y^2; dxy $\rightarrow$ dz^2 transitions respectively[333]. The assignments are based on octahedral symmetry with tetragonal distortion, the elongation being along the Z - axis[334]. The tetragonal radial parameters DS

Table - 17

Electronic spectral data and ligand field parameters of vanadyl complex.

Compound	observed bands	Assignments	10Dq (cm^{-1})	DS (cm^{-1})	Dt (cm^{-1})	L.F.S.E Kcals/mole
$[Vo(C_{10}H_{11}N_4O_3S)(H_2O)_2]$ Cl	12532	$dxy \rightarrow dxz, dyz(eg \rightarrow b_2g)$	12928	6920	-3864	-14.77
ueff = 1.8 B.M.	17107	$dxy \rightarrow dx^2 - y^2(eg \rightarrow a_1g)$				
	25460	$dxy \rightarrow dz^2(eg \rightarrow b_1g)$				

Fig 10 – I. R. Spectra of thio semicarbazide of 5 – acetyl – 2 – hydroxybenzoic acid .

$[C_{10}H_{12}N_4O_3S]$

Transmittance (%)

Wave number (cm⁻¹)

$[C_{10}H_{11}N_4O_3SiH_2O_2]_2Cl$
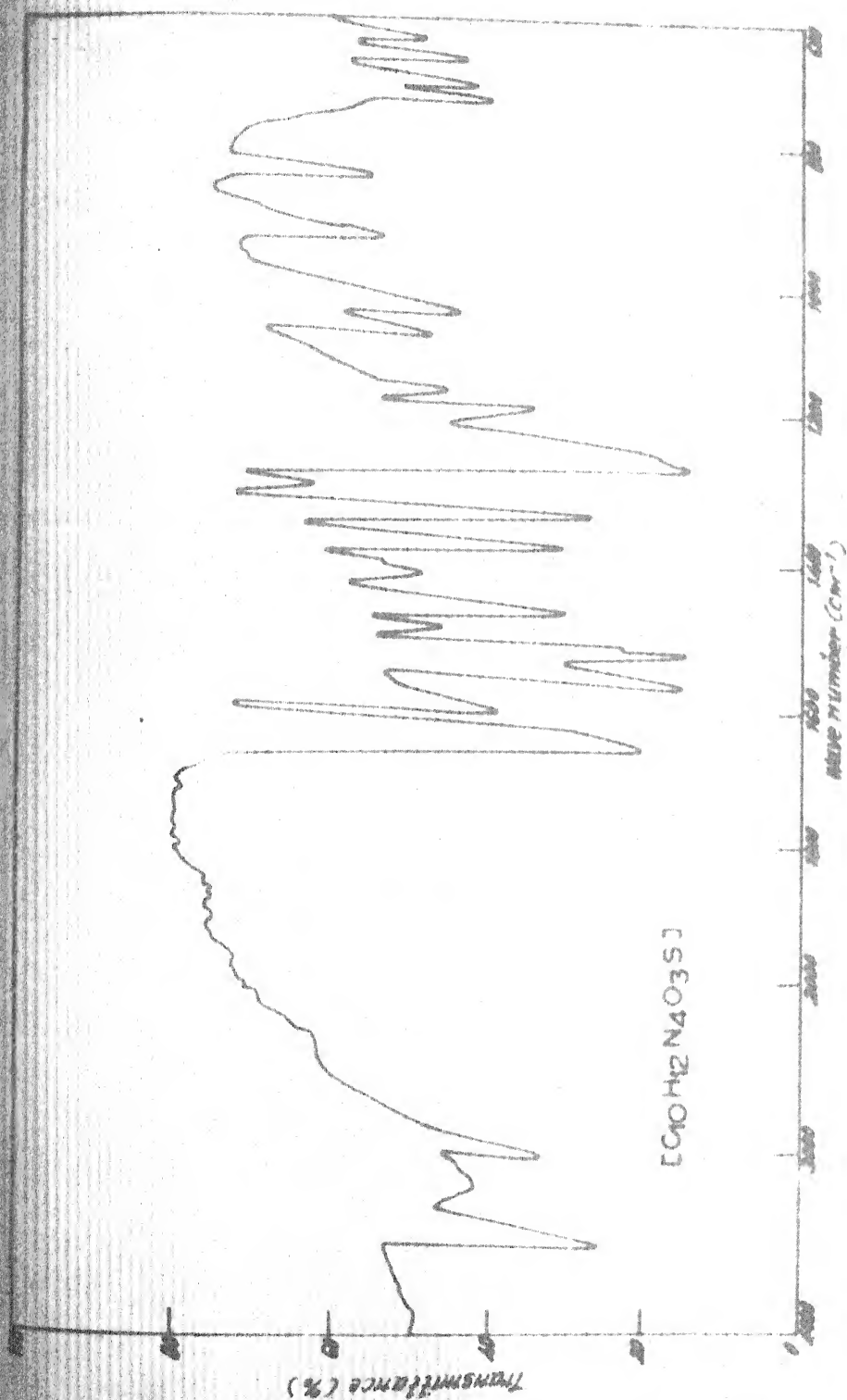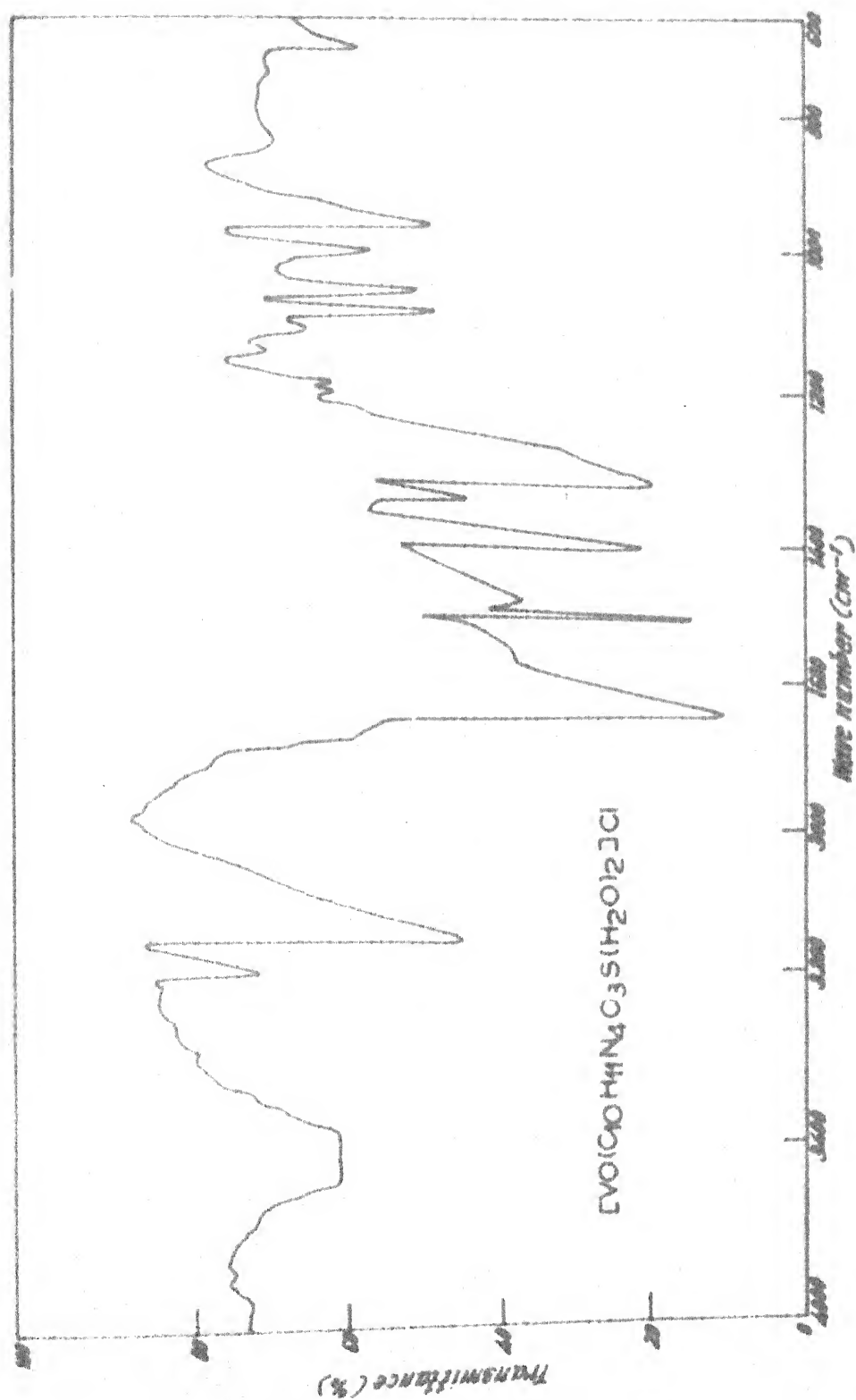
Fig.17

Table – 18

Infrared spectral assignment of Vo (IV) complex.

$(C_{10}H_{12}N_4O_3S)(5-AHBT)$	$\left[Vo(C_{10}H_{11}N_4O_3S)(H_2O)_2\right]Cl$	Assignments
3550(m)	–	–OH (Phenolic)
1350(S)	1320(S)	(C = S)
1290(S)	1310(S)	Phenolic mode (C – O)
–	980(m)	r(V = O)
–	3210(m)	r(NH)
1630(S)	3160(m)	amide I + NH bend
1615(S)	1640(S)	CH – bending
1540(m)	1500(m)	
1520(S)	1465(m)	NCS bend
1460(m)	1400(m)	
1075(w)	1070(w)	
1050(w)	1040(w)	$\int r(H_2O)$ coordinated
–	940(w)	
700(m)	695(m)	NH out of plane
Fig (10)	Fig (17)	

Section - IV

(A) Electronic, spectral and magnetic studies of rare earths complexes with Thiosemicarbazide of 1-hydroxy-2-naphthoic acid.

   (a) General Introduction

   (b) Method of preparation of thiosemicarbazide of 1-OH-2-naphthoic Acid

   (c) Rare earth complexes

(B) Antibacterial and antifungal activities of the alpha-benzamido-ortho chlorocinnamic acid and its metal complexes

Section - iv -

Electronic spectral and magnetic studies of rare earths complexes with thiosemicarbazide of 1-hydroxy-2-naphthoic Acid.

General Introduction :

Spectroscopic properties of the rare earths are very closely connected with magnetic susceptibility and paramagnetic resonance, so there discussion has a vital importance. As some rare earth ions are typical phosphors, the absorption and emission of fairly sharp lines may take place. The present knowledge of the energy levels was chiefly obtained from the analysis of the absorption and fluorescence spectra of the rare earth ions as well as complexes and in some cases fluorescence spectra with sharp lines in the visible and its neighbouring spectral regions were obtained[336,337]. In rare earths chelates, nitrogen coordinated complexes are rare because of the fact that nitrogen donating ligands would form unstable complexes and if the ligands are basic in character, would precipitate hydroxides of the metals.

Basically the coordination chemistry of lanthanide was of importance as it is related to the separation of these ions from each other and from this study it was observed that majority of such complexes are prepared from oxygen and nitrogen donor ligands and sulphur donor atoms seems to be lacking. Many authors[338-341] reported a

large number of complexes derived from weekly basic
uni- and multidentate amines in ethanolic medium.
Mehta[342-344] et al. studied the rare earth chelates of
tridentate Schiff bases.

In view of the fact that comparatively little
data is available in the literature on stereochemical
properties of lanthanide complexes, it was considered worth
while to study the electronic, spectral and magnetic
behaviour of some lanthanon complexes of thiosemicarbazide
of 1-hydroxy-2-naphthoic acid.

Method for the preparation of thiosemicarbazide of 1-hydroxy-2-naphthoic acid.

(I) Preparation of acid hydrazide :

Acid hydrazide of 1-hydroxy-2-naphthoic acid was
prepared by refluxing a mixture of the methyl ester of
1-hydroxy-2-naphthoic acid (1.0 M) hydrazinehydrate (1.5 M
99-100%) for three hours. The said hydrazide was recrystalised
from hot H_2O.

(II) Synthesis of thiosemicarbazide of 1-hydroxy-2-naphthoic acid :

A acid hydrazide of 1-hydroxy-2-naphthoic acid
(1.0 M) was suspended in liquor ammonia (d, 88 200ml) and
and CS_2 (45 ml cooled to $0^{o}C$) was added with stirring in
15 ml out of 45 ml portion. The temperature of the reaction

mixture was kept below 30°C by external cooling. Ethanol
(100 ml) 95% was then introduced into the flask. In
addition 30 ml of CS_2 was added followed by 100 ml of
ethanol (95%) when all the additions were complete the
reaction mixture which was kept in a water bath was stirred
with the help of a mechanical stirrer for an hour. An
aqueous solution of sodium monochloroacetate (1.0 M)
obtained by the neutralization of nomo-chloroacetic acid
with sodium carbonate, was then added and the heat was found
to develop to the warm solution. Hydrazine hydrate
(60 ml 99-100%) was added. After the reaction mixture was
shaken for ten minutes, it was filtered and the filtrate
was heated on a water bath to one half of its volume and cooled,
on cooling the concentrated reaction mixture overnight, crystals
of thiosemicarbazide of 1-Hydroxy-2-naphthoic acid were
obtained. The thiosemicarbazide was filtered, recrystallised
from glacial acetic acid - Molecular formula ($C_{12}H_{12}N_4O_2S$)
m.p. 68°C.

		C	H	N	S
Calculated %	–	52.17	4.35	20.29	11.59
Found %	–	53.87	4.28	21.14	11.07

Experimental :

Oxides samples were first converted into chloride
by dissolving the respective oxide into dilute hydrochloric
acid and the excess acid was removed by evaporation. The
ethanolic solution of 10 m. mole lanthanide (III) salts were

added into refluxing (20m mole) solution of the ligand in the same solvent in 1:2 ratio. The pH value of the vigorously stirred solutions were adjusted by drop wise addition of aqueous ammonium hydroxide to just below those for hydrous hydroxide or oxide precipitation. The solutions were then digested on water bath and the precipitated products were removed by filtration, washed, with water and dried in vacuo.

The elemental analysis of the complexes corresponds to the general empirical formula $\left[Ln(C_{12}H_{11}N_4O_2S)_2 \right] Cl\ H_2O$

Ln = La/Pr/Nd/Sm/Gd and Dy.

Results and discussion :

With the exception of Lanthanum (III) which is diamagnetic, all other complexes are paramagnetic. These values are quite in agreement with the values reported for typical lanthanide sulphate which suggest that the lanthanum and yttrium ions in the chelates act approximately as a free ion, as far as the f- electrons are concerned. In case of samarium (III) the experimental value is almost double the theoritical value. The reason for this is that in samarium, the first excited J-state is sufficiently close to the ground state causing an increase in the magnetic moment.

Fundamentally the spectral behaviour of the lanthanide is different from that of the transition metal

Table - 19

Analytical and magnetic data of Lanthanon (III) complexes with thiosemicarbazide of 1-OH-2-naphthoic Acid.

Compound	Chemical analysis % Calc./Found				u_{eff} expt. B.M.	* u_{eff} theoretical B.M.	** u_{eff} theoretical B.M.
	C	H	N	Cl			
La(C$_{12}$H$_{11}$N$_4$O$_2$S)$_2$] Cl. H$_2$O	38.79 (39.72)	3.23 (3.14)	15.09 (15.68)	4.78 (4.58)	0.20	0	0
Pr(C$_{12}$H$_{11}$N$_4$O$_2$S)$_2$] Cl. H$_2$O	38.69 (39.98)	3.22 (3.28)	15.05 (15.42)	4.77 (3.28)	3.65	3.58	3.62
Nd(C$_{12}$H$_{11}$N$_4$O$_2$S)$_2$] Cl. H$_2$O	38.52 (37.34)	3.29 (3.34)	14.98 (15.54)	4.75 (4.96)	3.68	3.62	3.68
Sm(C$_{12}$H$_{11}$N$_4$O$_2$S)$_2$] Cl. H$_2$O	38.20 (39.52)	3.18 (3.62)	14.86 (15.32)	4.71 (4.89)	1.50	0.85	1.55-1.65
Gd(C$_{12}$H$_{11}$N$_4$O$_2$S)$_2$] Cl. H$_2$O	37.86 (37.77)	3.15 (3.02)	14.72 (15.18)	4.67 (4.47)	7.85	7.94	7.94
Dy(C$_{12}$H$_{11}$N$_4$O$_2$S)$_2$] Cl. H$_2$O	37.60 (38.95)	3.13 (3.24)	14.62 (14.66)	4.63 (4.82)	11.00	10.64	10.60

* using curie formula

* Using simple spin orbit coupling,
** Using Van Vleck values.

ions. The reason for this difference is the fact that the electrons, which generates magnetic and spectral properties in lanthanide ions are 4f-electrons present in the 4f- orbitals which are effectively shielded from interaction with external forces by the overlapping of $5S^2$ and $5p^6$ electrons. The bands may be assigned to the transitions in which an f- electron is excited to an outer, d-, S- or p- orbitals and the spectra have been assigned to 4f $\rightarrow$ 5d transitions[345, 346].

Electronic spectra of the complexes taking the free ion as standard indicate the red shift[347] (nephelauxetic effect) which may be conveniently used as a measure of metal ligand covalent binding. The red shift or nephelauxetic effect according to Jorgensen occurs due to change in the interelectronic repulsion (Slater - Condon or Racah) parameters.

The nephelauxetic ratio β is defined as

$$\beta = \frac{F_k^c}{F_k^f}$$ where the F_k^c and F_k^f are the Slater - Condon

parameters for the complex and the free ion respectively, this may be also defined[348-350] as $\beta = \frac{V_c^-}{V_f^-}$

where V_c^- and V_f^- are energies (in cm^{-1}) of the transitions in complex and free ion respectively. The values of β is calculated using above equation and taking into account as many transitions as possible. The mean β value, $\bar{B}$ can be used to calculate a new parameter of bonding (δ) in percent

which is given as $\delta = \left(\dfrac{1 - \beta}{\beta} \right) \times 100$

The value of δ – may be positive or negative depending upon the ligand. Positive value of δ indicate covalent bonding where as the negative value of δ shows ionic bonding.

Choppin[351] correlated the bonding parameter $b^{\frac{1}{2}}$ to the nephelauxetic ratio by the relationship,

$b^{\frac{1}{2}} = \left[\left(\dfrac{1 - \beta}{2} \right) \right]^{\frac{1}{2}}$. The value of parameter $b^{\frac{1}{2}}$ indicates the

extent of 4f– participation in the complexation. Greater the magnitude of this parameter greater is the contribution of 4f– orbital to complex formation. The positive value of δ and $b^{\frac{1}{2}}$ and less than unity values of β in the present complex points towards the incidence of covalency in the metal ligand bond.

IR – studies :

The IR spectra of the rare earth complexes and the ligand is given in table (21). The assignments of the important bands are based on corresponding thiosemicarbazide, thiosemicarbazones and the complexes derived from them. The free ligand exhibits band around 3510, 1740, and 1300cm^{-1}, which can be assigned to pehnolic –OH; amido CONH and (C = S) groups. In the metal chelates the frequencies of r(C = S) and r(CONH) have lowered considerably and the frequency of

Table - 20

The energy (in cm^{-1}) of the bands and calculated values of Nephelauxetic ratio and bonding parameters of Lanthanon complexes:

Levels	Pr^{+3} ion free ion	complex	Nd^{+3} ion Levels	free ion	complex	Sm^{+3} ion Levels	free ion	complex	Gd^{+3} ion Levels	complex
1D$_2$	16480	16300	4G$_{5/2}$	17100	17300	4F$_{3/2}$	18680	19320	8S$_{7/2}$ $\rightarrow$ 6P$_{7/2}$	32850
3Po	21320	20640	4G$_{7/2}$	19000	19080	4G$_{7/2}$	20000	19840	8S$_{7/2}$ $\rightarrow$ 6I$_{9/2}$, I$_{17/2}$	36430
3P$_1$	22460	22180	4G$_{9/2}$	19340	19580	4I$_{11/2}$	20980	20960		
3P$_2$	23260	22400	2G$_{9/2}$	21004	21000	4I$_{12/2}$	21580	21530		
						4G$_{9/2}$	22780	22530		

$\bar{\beta} = 0.97$
$\delta_{\frac{1}{2}} = 3.09$
$b^{\frac{1}{2}} = 0.122$

$\bar{\beta} = 1.00$
$\delta_{\frac{1}{2}} = 0$
$b^{\frac{1}{2}} = 0$

$\bar{\beta} = 0.99$
$\delta_{\frac{1}{2}} = 1.001$
$b^{\frac{1}{2}} = 0.07$

-OH disappears indicating involvement of (C = S) and amido nitrogen and phenolic (OH) in complexation. New bands near 3300 and 1600 cm^{-1} in the complexes have been assigned to r(O-H) and δ H$_2$O vibrations of the water molecule.

Fig.16.- I.R.Spectrum of thio semicarbazide of 1 -OH - 2 - naphthoic acid .

[C2H2N4O2S]

Wave number (cm⁻¹)

Transmittance (%)

Cla(C12H11N4O2S)2Cl·H2O

Fig.50

[Pr(C₂H₄N₄O₂S)₂₃]Cl·H₂O

Fig.20

Transmittance (%)

CN⁻ (C₂H₅)N₄O₂S)₂CD₃ H₂O

Wave number (cm⁻¹)

Fig. 2.

[Sm(C2H11N4O2S)2Cl]·H2O

Fig-22

[Gd (C2H11 N4O2 S)2Cl]·H2O
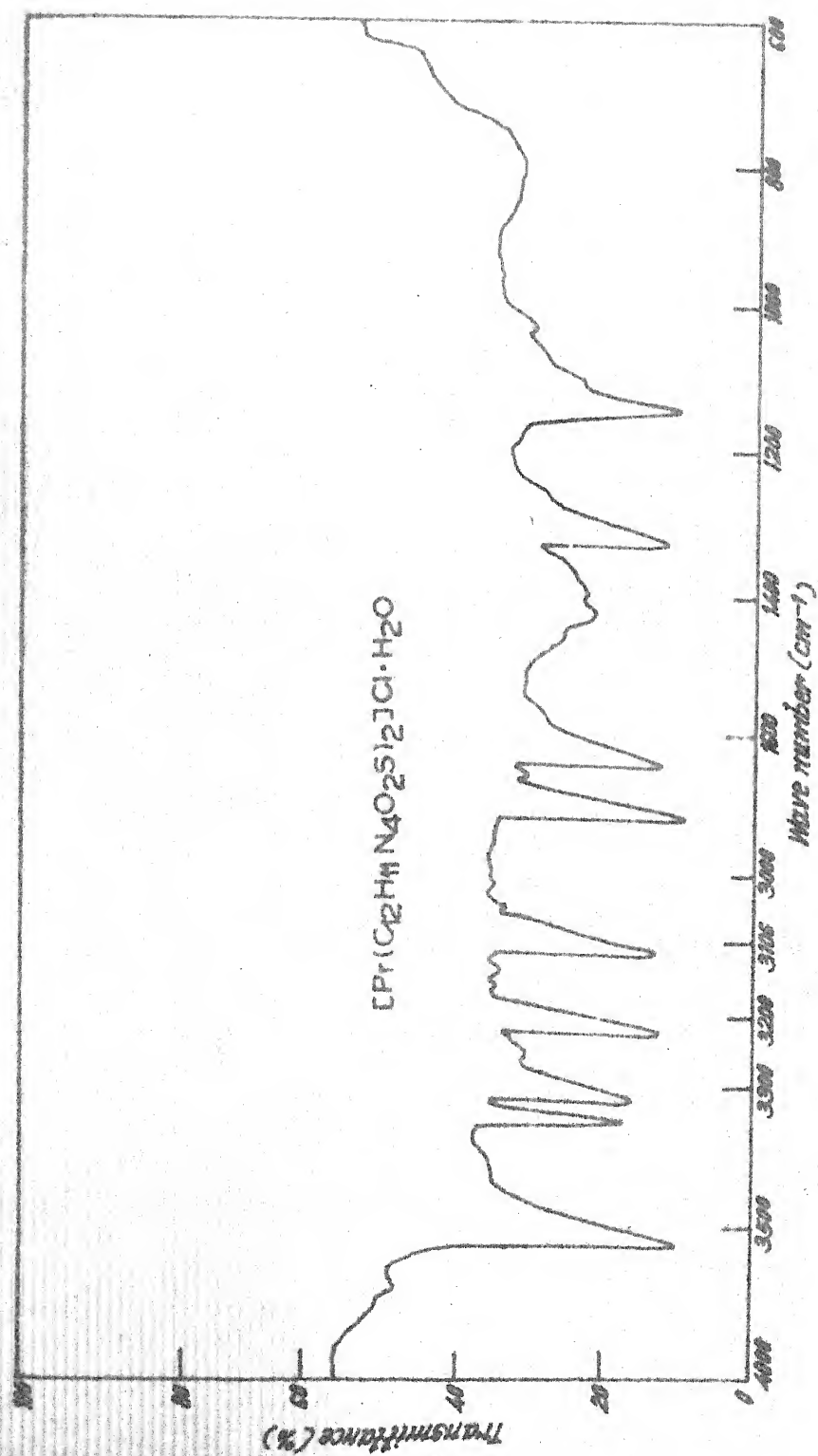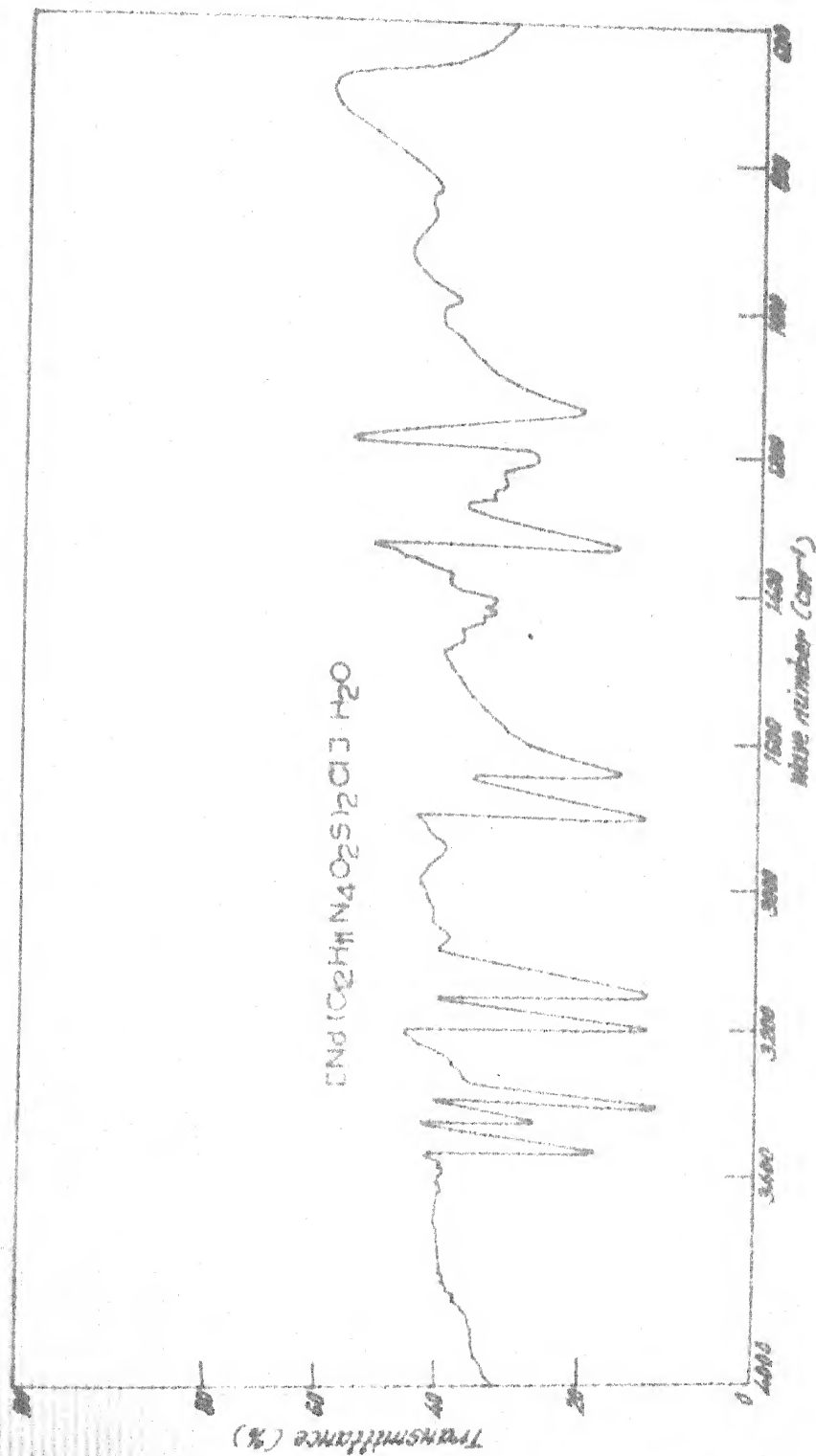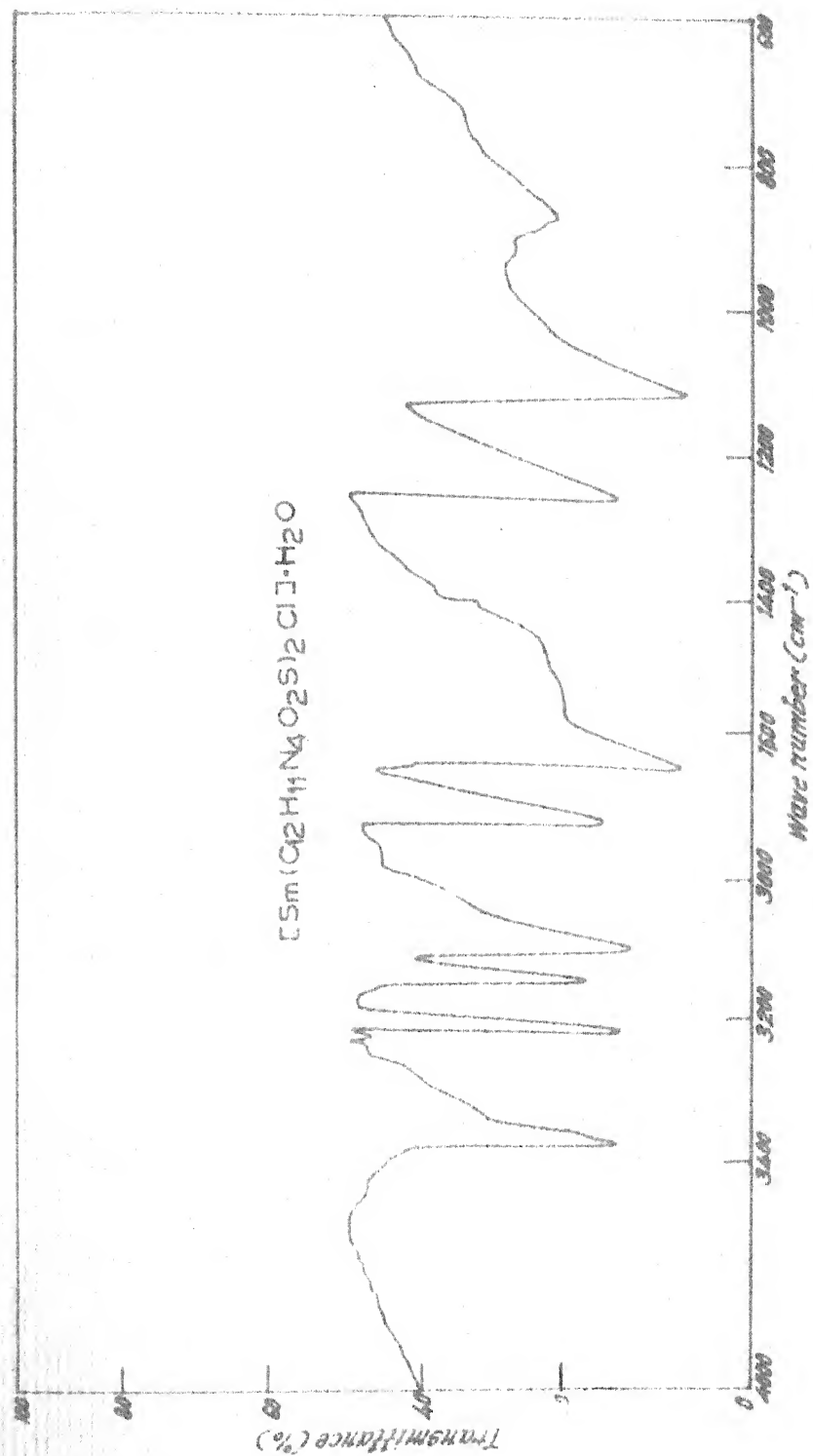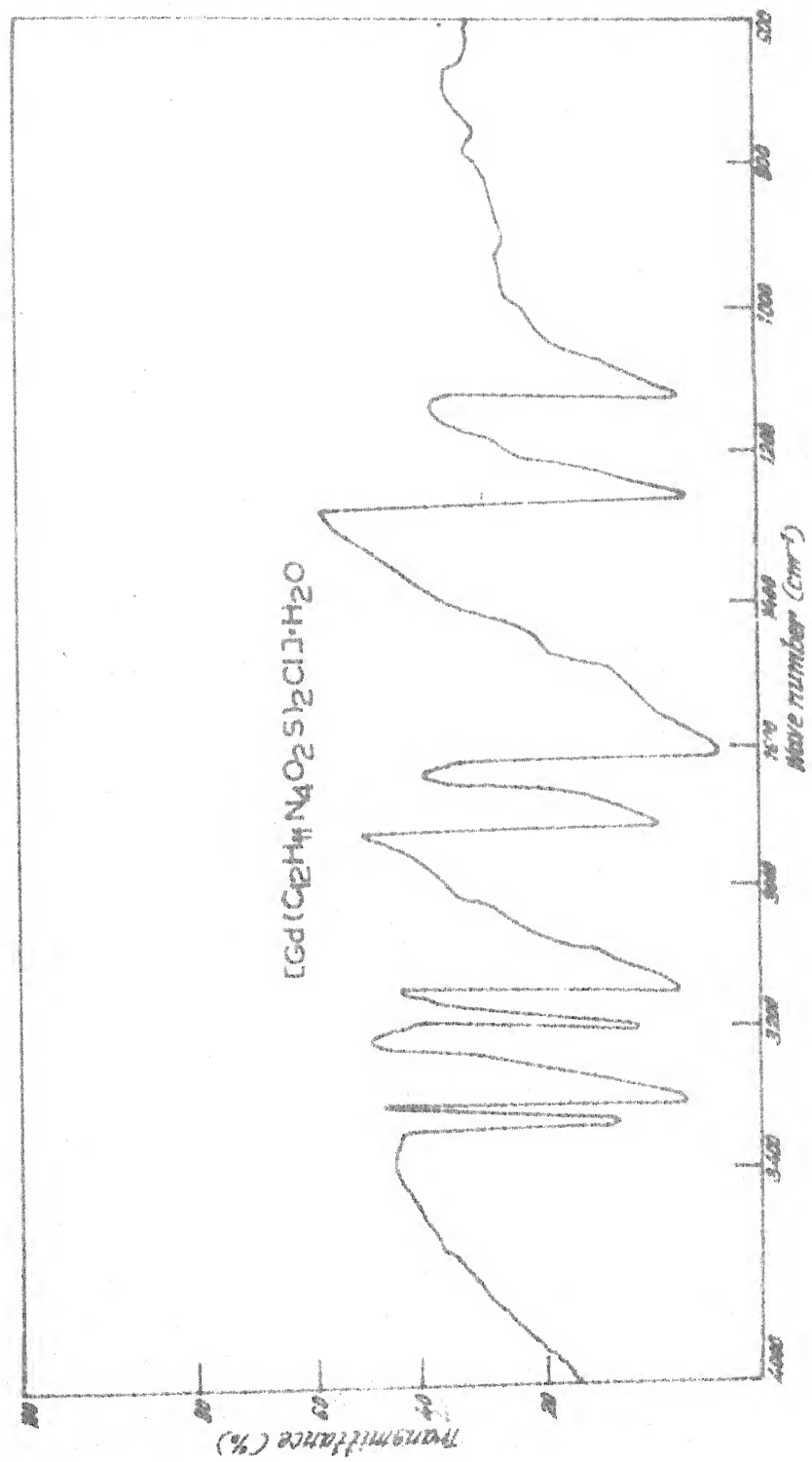
Fig-23

Table - 21

Infra red spectral assignment of Lanthanons complexes (Thiosemicarbazide of 1-OH-2-Naphthoic Acid.

(HNAT) $(C_{12}H_{12}N_4O_2S)$	$[La(C_{12}H_{11}N_4O_2S)_2]$	$[Pr(C_{12}H_{11}N_4O_2S)_2]$	$[Nd(C_{12}H_{11}N_4O_2S)_2]$	$[Sm(C_{12}H_{11}N_4O_2S)_2]$	$[Gd(C_{12}H_{11}N_4O_2S)_2]$	Assignments
	Cl.H$_2$O	Cl.H$_2$O	Cl.H$_2$O	Cl.H$_2$O	Cl.H$_2$O	
3510	-	-	-	-	-	r(OH) Phenolic
1300	1280	1310	1315	1270	1270	r(C = S)
1740	1700	1710	1700	1710	1720	r(CONH)
3400(S) 3200(S) 3160(S)	3370(S) 3190(S) 3150(S)	3340(S) 3210(S) 3100(S)	3380(S) 3200(S) 3150(S)	3370(S) 3190(S) 3150(S)	3340(S) 3200(S) 3150(S)	r(NH+NH$_2$)
1120(m)	1130(m)	1130(m)	1120(m)	1125(m)	1120(m)	r(N-C-N)
-	3560(S) 3240(S)	3510(S) 3310(S)	3330(S) 3310(S)	3210(Sb)	3310(Sb)	r(OH) of H$_2$O
-	1660(m)	1630(m)	1640(mb)	1630(m)	1630(m)	r(OH) of H$_2$O
Fig (18)	Fig (19)	Fig (20)	Fig (21)	Fig (22)	Fig (23)	

Antibacterial and antifungal activities of the α-benzamido-ortho-chloro-cinnamic acid thiosemicarbazone and its metal complexes.

Introduction :

The drugs which are used to destroy the bacteria responsible for the diseases are known as antibacterial compounds. Numerous complexes of thiosemicarbazide and thiosemicarbazones have been reported in literature[352-360]. Not merely their use in analytical processes or behaviour as pesticidal and fungicidal but also the activities of such reagents and some of their chelates against many diseases. The remarkable antituberculous activity of isonazid has initiated substantial amount of reserach[361,362] on the transition metal complexes of pyridine carboxylic acid hydrazides and their derivatives.

The chemical used to wage war against fungi are known as fungicides. The term fungicide is firmly established in practice to control the damage caused by fungi. The effect may be kill or check the growth or to prevent sporing of the fungus. Action of the fungicides are specific. A number of thiohydantion derivatives are physiologically active and some of them have been reported to possess anticonvulsant[363], antibacterial[364], antifungal[365], antihypertensive[366] and such other properties.

The group $\rangle N - \underset{|}{C} = S$ is of considerable chemotherapeutic interest and is responsible for pharmacological activity[367]. It is presumed that the microbiol activity of thiosemicarbazones is due to their ability to chelate traces of metals[368]. Synergistic effect of combination of different antibiotics with metallic compounds have been reported by several workers[369,370]. Mercury is highly toxic because it combines with cellular metabilite containing SH- groups and thus depriving the cell of those metabillites as a result of which the cell dies[371].

In view of antituberculosis[372] and other pharmacological[373-378] activities of metal thiosemicarbazides in biological systems, the physicochemical studies of the metal complexes are desired.

Encouraged by the earlier findings it was thought worth while to synthesise and characterise some thiosemi-carbazones and their metal complexes with first row transition metal series with a view to study the antibacterial and antifungal activities of these compounds. In the present work the antibacterial and antifungal activities of the ligand α-benzamido-o-chlorocinnamic acid thiosemicarbazone and its metal complexes with first row transition metal have been evaluated in vitro against the bacteria Staphylococcus aureus and Escherichia coli and Fungi Helminthos porium sativum and Altemaria altemata .

<u>Method for bacteria</u> :

The bacterial cultures tested in present investigations were collected from I.A.R.I. Pusa New Delhi and were maintained by periodic transfer on <u>Potatodextose</u> <u>agar</u> (PDA) incubated at 30°C. For testing the <u>invitro</u> activity of the compounds each species was grown at room temperature for 48 hrs in liquid medium of the composition

> Beef extract - 3.0 gm
>
> Paptone   - 10 gm
>
> Yeast   - 5.0 gm
>
> Distilled water - 1 litre
>
> pH - 7

0.1 mg of the compounds were dissolved in 10 ml acetone. One ml of sufficiently uniform and profuse growth of each species obtained after 40-48 hours incubation was added to the nutrient agar medium of the same composition as the liquid medium mentioned above but with the addition of 2% agar in separate conical flask at 30°C and was thoroughly mixed by gentle shaking and cooled. 3.0 ml of the contents of a flask were evenly spread in a petridish (10 cm in diameter) and allowed to settle for two hours.

After hardening of agar the compounds were tested by Agar diffusion method[379]. In a cups 0.1 mg/10ml of a solution of the compound in acetone by means of a sterile 1 ml pipette were taken. The suitable control containing

the same volume of acetone was maintained to ascertain the
inhibitory effect of the solvent. The petridishes were
incubated in refrigerator at 5°C for two hours to permit the
diffusion of the antibiotic in agar. At the end of this
period the dishes were taken out and incubated at 28-30°C
for 48 hours. After this the dishes were taken out and
zone of inhibition as a diameter of each spot was measured
in mm after 24 hours. The difference of diameter of the
zone of inhibition as a diameter of each spot was taken out
and zone of inhibition of the test solution and that of the
control gives the actual diameter of the zone of inhibition
of the rest compounds.

The measurements were done in triplicate and
average measurements are given in table (22).

Method for fungi :

100 ml of a standard 2% potatodextrose agar medium
was dispensed into 250 ml. Erlenmeyer flasks are sterilized
by autoclaving at 10 lb pressure at 150°C for 10 mts. To each
of flasks 10 ml of acetone containing 0.01, 0.02, 0.05 and
0.10 mg of the compounds were added. After homogenous
stirring, the samples were taken out in a big petridishes.
After the medium was set the petridishes were inoculated with
5 mm disc cut from the outer margin of cultures of H. sativum
and A. alternata growing on PDA and placed in the centre of
the petridishes in an inverted position in direct contact

with the medium and incubated at $25 \pm 1^{\circ}C$. After culturing
the disc for some time, some amount of acetone is added
to ascertain that the solvent does not produce any inhibitory
effect on inoculum.

After a week a linear growth of the fungus was
obtained by measuring the colony diameters. Average of the
growth was taken. The amount of the inhibition was
calculated using the formula

$$\text{Percentage of inhibition} = \frac{(C - T) \times 100}{C}$$

where C- diameter of fungus colony in control plate after
7- days.

T - fungus of fungus colony in test plates.

Observations and Discussion :

The zone of inhibition measured against the
micro organism S. aures and E. Coli indicate that S. aures
is more positive to these compounds where as E. coli shows
resistance.

Chromium complex is more active fungicides, where
as other complexes are not much fungitoxic to this particular
fungi.

Table – 22

Antibacterial activity of α-benzamido ortho chlorocinnamic acid and metal complexes against the bacterias E. coli and S. aureus.

Zone of inhibition in millimeter

Compound	S. aureus		E. coli	
	24 hrs	48 hrs	24 hrs	48 hrs
BCCA	20+	20+	20+	16+
$Co(C_{17}H_{16}N_5O_2ClS)Cl_2$	10±	9±	9±	10±
$Ni(C_{17}H_{16}N_5O_2ClS)(SO_4)H_2O$	11±	10±	10±	11±
$Cu(C_{17}H_{16}N_5O_2ClS)Cl_2H_2O]H_2O$	13±	14±	12±	+13
$Cr(C_{17}H_{16}N_5O_2ClS)Cl_3$	15+	12+	12±	+13
$Fe(C_{17}H_{16}N_5O_2ClS)Cl_3]2H_2O$	15+	10+	10±	8±

+   Indicate sufficient inhibition.

±   Indicate partial inhibition.

Table - 23

Growth response after a week on PDA medium of H. sativum and A. alternata at different concentrations.

Compound	Percentage inhibition at different concentration							
	H. sativum				A. alternata			
	0.01	0.02	0.05	0.1	0.01	0.02	0.05	0.1
BCCA	40	50	67	80	42	51.7	70.1	78
$[Co(C_{17}H_{16}N_5O_2ClS)Cl_2]$	38.2	43.7	61.8	70.3	31.0	40.2	60.4	66.4
$[Cr(C_{17}H_{16}N_5O_2ClS)Cl_3]$	43	52	67.8	82	41	50	68.2	72.4
$[Fe(C_{17}H_{16}N_5O_2ClS)Cl_3]2H_2O$	29.5	45	50	60	22	32	40.7	56.0
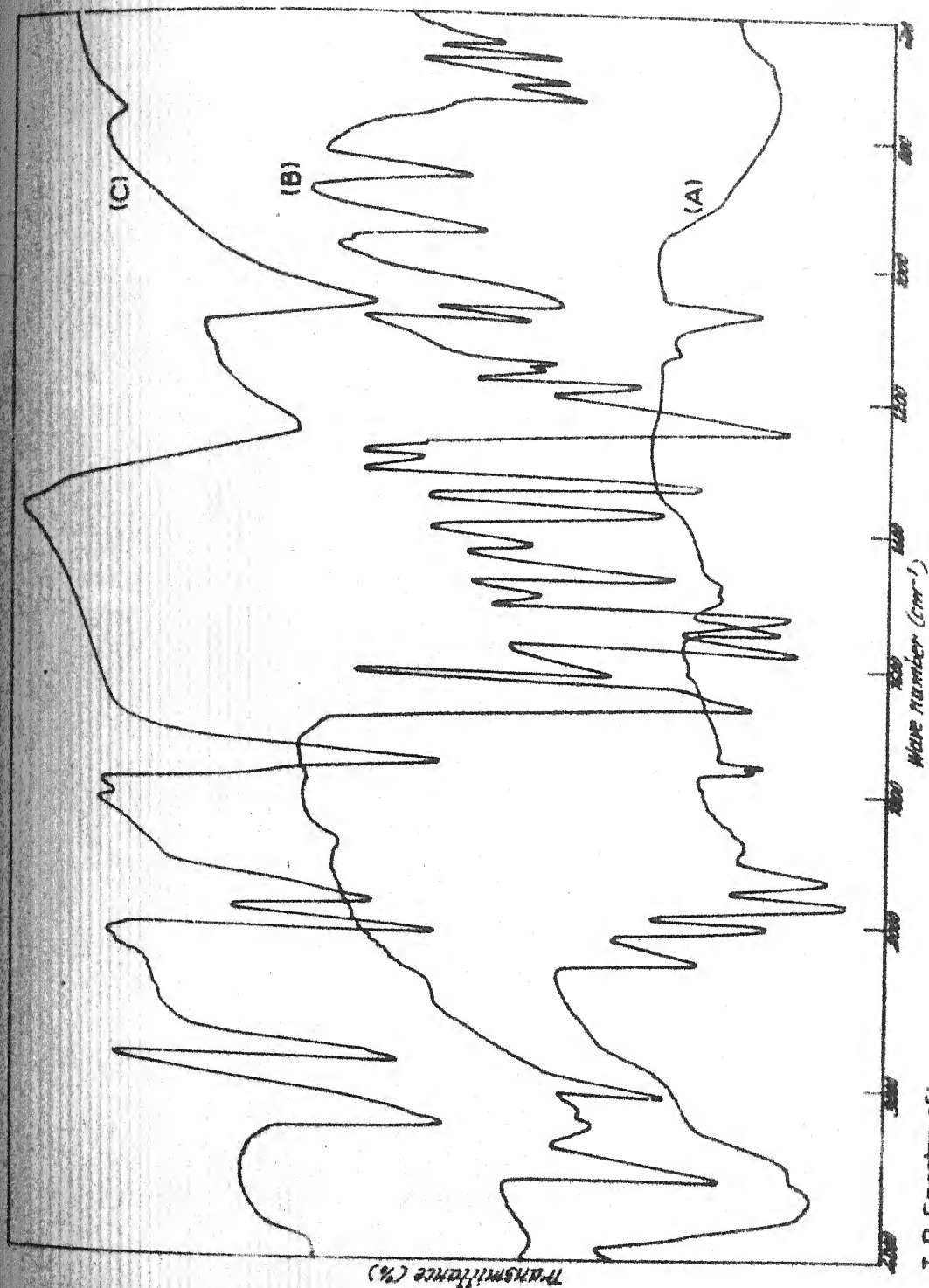
I.R. Spectra of:

(A) – Thio semicarbazide of ∝ – benzamido – o – chlorocinnamic acid.
(B) – Thio semicarbazide of 5-acetyl-2-OH-benzoic acid.
(C) – Thio semicarbazide of 1-OH-2-naphthoic acid.

Infra red spectral bands of thiosemicarbazedes.

Thiosemicarbazide of α-benzanido-o-chloro-cinnamic acid	Thiosemicarbazide of 5-Ac-2-OH-Benzoic acid	Thiosemicarbazide of 1-OH-2-Naphthoic acid	Assignments
1620-1640	1680(Sb)	1670(Sh)	-CONH
1230(S) 850(m)	1350(S)	1350(S)	-C = S
1610(S)	1600(S)	1600(Sh)	-NH-NH$_2$
1700(S)	-	1630(w)	NH-C-C$_6$H$_5$ $\overset{\|}{O}$
-	3545(S)	3510(S)	-OH
-	1650(m)	-	-COCH$_3$
1540(S)	-	-	amide I
1280(w)	-	-	amide III
Fig (A)	Fig (B)	Fig (C)	

105(A)

Section - V

A. Physical measurements and analytical estimations

B. Methods of calculation

C. References

D. Resume

Physical Measurements and Methods of calculation

Physical Measurements :

(a) Magnetic Measurements :

  The magnetic susceptibility of the isolated complexes were measured in powder form using Guoy's balance. Mercury (II) tetrathiocyanato cobaltate (II) $\left[HgCo(CNS)_4\right]$ (X_g = 16.442 X 10^{-6} CGS unit at $293^{\circ}A$) was used as calibrant. Tube constant was calculated from time to time to check the satisfactory working of the apparatus. The measurements were carried out in the department of chemistry, Delhi University, Delhi and T.I.F.R., Bombay.

(b) Infrared spectral studies :

  Infrared spectra of the compounds were recorded on a Perkin-Elmer 621 spectrophotometer in KBr Pellets. These measurements were carried out at C.D.R.I., Lucknow, Modi Pon Ltd., Modinagar and Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras and I.G.F.R. Institute, Jhansi.

(c) Electronic spectral measurements :

  The electronic spectra of the complexes were measured in non aqueous media using Bausch and Lomb spectronic 20 and Perkin-Elmer 621 spectrophotometer at room temperature.

(d) pH- Measurements:

pH- measurements were made at room temperature on an Elico pH-meter using glass electrodes.

(e) Chemical analysis :

The metal contents in all the complexes were estimated as follows :

A known weight of the complex was decomposed with a mixture of conc. HNO_3 and H_2SO_4 by heating. The organic matter was filtered and the residue was dissolved in doubly distilled water or sometimes dilute hydrochloric acid was added to it and made upto a known volume, from which the metal contents were estimated by standard literature methods. The micro analysis of carbon, hydrogen and nitrogen for the ligands and the isolated complexes was done at Modi Steels, Modinagar, Modi Rubber Ltd., Modi Puram (Meerut) and I.G.F.R. Institute, Jhansi.

Ligand Field Parameters :

The various ligand field parameters such as Dq, Dq^{xy}, Dq^z, Ds, Dt, Angular overlap parameters such as $d\sigma$, $d\pi$, $e\sigma^1$, xy^2, $e^1\sigma z$, $e^1\pi xy$, $e^1\pi z$ and normalised spherical parameters e.g. DS, DT, DG, Dq^{xy} and DQ^z have been calculated by literature methods[380-383].

Magnetism :

Magnetic susceptibility (using Guoy's balance)

has been calculated using the formula

$$\beta = \frac{16.44 \times 10^{-6} \times \text{Room temperature } K^{o} \times W}{\text{Temperature } K^{o} \times \triangle W^{1}s}$$

$\triangle W^{1}s = (\triangle Ws - \mathcal{E}W)$

$\mathcal{E}W$ = the change in the weight of the empty tube.

$\triangle s$ = the change in weight of the calibrant.

W = weight of the calibrant

$$Xg = \frac{B \times \triangle WT}{W}$$

Xg = gram susceptibility of the complex.

B = tube constant.

W = weight of the complex.

$\triangle WT$ = change in the weight of the complex.

$\text{ueff} = 2.828 \sqrt{XM \times 10^{-6} \times T}$

ueff = magnetic measurement at temperature (T).

XM^{1} = molar susceptibility corrected for dimagnetism
(according to the value suggested by Figgis and
Lewis).

T = absolute temperature

The magnetic susceptibility measurements[384]
were carried out by the Guoy method using a thin Pyrex glass
tube (1.2 cm an internal diameter and 15 cm long).

The calibration of the balance was done by using

conductivity water and this water was also used as refrence solvent. All susceptibility measurements were carried out at room temperature.

Covalency factor or Nephlauxetic Ratio :

Covalency factor (β) has been calculated by using the relation $\beta = \dfrac{B \text{ (in complex)}}{B \text{ (in free ion)}}$. The value of $\beta = 1.0$ indicate 100% ionic character while $\beta = 0.5$ indicate 100% covalent character. Thus the values β = between 0.5 and 1.0 clearly suggests the partial covalency character.

Ligand field splitting energy (10Dq or $\triangle$) :

It is the orbital separation energy between Vg or t_2g and V_3 or (eg) often represented by 10Dq or $\triangle$. In all the systems 10Dq has been calculated using the equations suggested by Figgis[385] and Ballhausen[386].

Recah's Inter- Electronic repulsion parameters :

Where the interaction between two or more electrons are involved, it is possible to write down the energy for each term above the ground term, which arises as an expression involving several parameters. The energies are a function of the electron repulsion parameters. The two parameters can be choosen either the condon shortly. Parameters F_0, F_2, F_4) or the Recah's interelectronic repulsion parameters[387-389] (A,B,C). These parameters are sufficient if attention is restricted to d- electrons. Excitation

energies of some multiple terms in spherical symmetry
expressed in Racah parameters (B) and (C) of inter electronic
repulsions are given below in table (24 and 25).

Table - 24

Relevent excitation energies of some of the terms for d^n
configuration are given below :

Ground term	d^5	Ground term	$3d^3$ & d^7	Ground term	d^2 & d^8
6S	O	4F	O	3F	O
4G	10B + 5C	2G	4B + 3C	1D	5B + 2C
4P	7B + 7C	4P	15B	3P	15B
4D	17B + 5C	2P	9B + 3C	1G	12B + 2C
4F	22B + 7C	2H	9B + 3C	1S	22B + 7C

Table - 25

Free ion values of B and C for different gaseous [390,391]
ions based on electronic configuration.

Electronic configuration	Ion	B	C
$3d^2$	V^{+3}	816	4165
$3d^3$	Cr^{+3}	918	3850
$3d^4$	Mn^{+3}	1140	3675
$3d^5$	Mn^{+2}	968	3525
$3d^6$	Fe^{+2}	1058	3901
$3d^7$	Co^{+3}	1100	–

Table 25 continued.

Electronic configuration	Ion	B	C
$3d^8$	Co^{+2}	971	4366
$4d^6$	Ni^{+2}	1041	4831
$4d^8$	Rh^{+3}	720	-
$5d^4$	Pd^{+2}	683	2620
	Ce^{+4}	700	-
$5d^6$	Ir^{+3}	600	-
	Pt^{+4}	720	-
$5d^8$	Pt^{+2}	600	-

Ligand field stabilisation energy :

Ligand field stabilisation energy is simply given by the energy gain in units of Dq for the ground states. Following table represents the value of L.F.S.E. For different electronic configurations. Actually L.F.S.E. is known as the difference between the lowest energy level of a term split by a ground field and the centre of gravity of the term in the ligand field.

Table - 26

L.F.S.E. Values of different electronic configurations :

Electronic configuration	L.F.S.E. for octahedral complexes	
	Weak field	Strong field
d^1	4Dq	4Dq
d^2	6Dq	$8Dq - (3F_2 - 15F_4)$
d^3	12Dq	12Dq
d^4	6Dq	$16Dq - (6F_2 + 145F_4)$
d^5	ODq	$20Dq - (15F_2 + 275F_4)$
d^6	4Dq	$24Dq - (5F_2 + 255F_4)$
d^7	6Dq	$18Dq - (7F_2 + 105F_4)$
d^8	12Dq	12Dq
d^9	6Dq	6Dq

$$L.F.S.E. = \frac{X. Dq}{350} \quad (X - \text{varies according to } d^n \text{ configuration})$$

Spin orbit coupling constant (λ) :

The spin orbit coupling constant for the ions where complete quenching is expected has been calculated using the formula

$$u = u_0 \left(1 - \alpha\lambda/10Dq \right)$$

where u = observed magnetic moment in B.M.

u_0 = spin only moment in B.M.

α = A constant, (4 for F- ground state ion and 2- for D-ground state ion).

10Dq= Ligand field splitting energy.

Lande's splitting factor (G) in octahedral fields :

The value of Lande's splitting factor has been calculated by the given formula

$$G = \left[\frac{(2 - 8\lambda)}{10Dq} \right]$$

where λ = spin orbit coupling constant.

10Dq = Ligand field splitting energy.

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List of Publications

1. Thermodynamic and stability constants of Cu^{+2}; Fe^{+2}; Ni^{+2} and Co^{+2} complexes with 5-sulfo-salicylic Acid. Thermochim. Acta (accepted for publication)

2. Magnetic, electronic and spectral studies of transition metal complexes of thiosemicarbazide of alpha-benzamido-ortho-chlorocinnamic Acid.
   Jour. Ind. Chem. Soc. (communicated).

3. Some novel coordination compounds of rare earth ions with 5-acetyl-2-OH-benzoic acid thiosemicarbazide.
   Jour. Ind. Chem. Soc. (communicated).

4. Antibacterial and antifungal studies of transition metal complexes of thiosemicarbazide of alpha-benzoamido-o-chlorocinnamic Acid.
   Jour. Ind. Chem. Soc. (communicated).

5. Magnetic and electronic spectral studies of Fe^{+3}, Co^{+2} and Ni^{+2} complexes of 1-OH-2-naphthoic Acid thiosemicarbazide.
   Jour. Ind. Chem. Soc. (communicated).